Grading Characteristics of Texaco Gasification Fine Slag: Quality Distinction and Selective Distribution of Trace Elements

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ABSTRACT: Aiming at hard-to-reuse gasification fine slag, a new process of treating gasification fine slag by classification was presented. The screening treatment was carried out based on ensuring the original particle size composition of fine slag, and it was divided into six particle size ranges as follows: +0.5, 0.3−0.5, 0.125−0.3, 0.074−0.125, 0.045−0.074, and −0.045 mm. The physical properties of different size range samples were examined by elemental analysis, X-ray diffraction, X-ray fluorescence, cold field emission scanning electron microscopy, and energy-dispersive spectrometry. The results showed that the carbon content of the median section (0.125−0.3 mm) fine slag had significant improvement compared with the other section fine slag. The carbon distribution of the +0.125 mm fine slag was concentrated, while the carbon distribution of −0.125 mm was dispersed and closely mixed with minerals. The content of trace elements Cr, Mn, Ni, V, Cd, Pb, and Mo was determined by inductively coupled plasma−mass spectrometry, and the correlation between minerals and trace elements of different particle size-graded fine slag was evaluated by Pearson correlation analysis. The results suggested that high vaporization temperature and metallic oxide forms of trace elements had a strong correlation with feldspar.

1. INTRODUCTION

The entrained flow gasification processing is the most widely used gasification technology in China. Especially, the Texaco gasifier dominates applications in northwest China because of its stable feedstock and operation. However, the solid waste of gasification was difficult to process and has resulted in the deposition of a large amount of gasification slag. According to relevant statistics, emissions of gasification slag in China, 2011, ranged from 18 to 32 Mt.1 Texaco gasification slag is composed of coarse slag and fine slag, which have distinct gasification processes and subsequent treatment processes (as shown in Figure 1). The coarse slag was obtained by discharging the molten slag from the bottom of the gasifier and then cooling in the chilling chamber and slag pool. The gasification fine slag originated from the particles carried by syngas, which were separated in a scrubber tower. Then, the black water in the scrubber was dehydrated to form fine slag. The carbon content of coarse slag is extremely low (less than 5%), but the carbon content of fine slag is higher than that of coarse slag.2 Gasification coarse slag is often used for landfill treatment or as a building material.3 However, because of the peculiar carbon content in fine slag, its use as a landfill or a building material does not meet the fire loss standards and its calorific value does not meet the requirement when it is used as a fuel for power generating boilers.

In the northwest of China, because of the geological conditions, the hazardous trace element content of coal is relatively high compared with that in other regions.4 Therefore,
in addition to the process of transformation and utilization, its industrial solid waste may also cause pollution to soil and water resources without proper handling. The treatment and utilization of fine slag have become a difficult problem in the coal chemical industry.

At present, some scholars have studied the gasification fine slag or the trace element content and occurrence form of solid waste from coal conversion. Matjie et al.\(^{5,6}\) investigated the characteristics of unburned carbon particles in gasification slag. The high-carbon particles in the coarse slag of the fixed bed had a large particle size (4–13 mm) and high-density carbon structure with low sulfur content. Pan et al.\(^{6}\) studied the differences for pore structure, carbon content, and crystal structure of coarse and fine slag with entrained flow pulverized coal gasifier. In addition, the pore structure of high-carbon particles was developed, which was a high-quality raw material for the preparation of activated carbon. Zhao et al.\(^{7}\) studied the morphology and reactivity for coarse and fine slag of entrained flow gasification. The morphology of carbon in fine slag appeared as a loose flocculent, and the gasification reactivity of fine slag is higher than that of coarse slag. Huo et al.\(^{8}\) conducted the gasification characteristic of a small amount of gasification fine slag mixed with raw coal. When the gasification slag exceeded a certain amount, it would hinder the gasification reaction. Ge\(^{9}\) studied the flotation extraction of gasification fine slag, but the flotation effect was not ideal and the dosage of collecting agents was large. The current research on trace elements of coal and coal combustion ash focuses on the content, occurrence form, and thermal stability. Bhangare et al.\(^{10}\) studied the distribution and enrichment of trace elements in combustion coal ash. They found that Mn was the most abundant and the enrichment degree of trace elements in fly ash was higher than that in bottom ash. The leaching of fly ash shows that Pb, Ni, Cr, Mo, V, and Cd had high mobility.\(^{10–13}\) This indicates that these trace elements are easy to transfer from solid waste to soil and water. Tang et al.\(^{14}\) studied the leachability of 16 kinds of trace elements in gasification slag. Comparing coarse slag and fine slag, the leachability of partial trace elements was different.

The wide studies have shown that the high-carbon component in gasification fine slag has a high utilization value. However, the separation cost of organic matter in fine slag is exorbitant, the direct utilization effect of original fine slag is not ideal, and hazardous trace elements in solid waste may lead to secondary pollution. In this work, the distribution regularity among the particle size, component, and structure of fine slag were presented. High-carbon components and high-ash components in fine slag were separated effectively by screening. The correlation among particle size, hazardous trace elements, and mineral components in gasification fine slag were studied. Meanwhile, we found that the fluctuation of trace element content changed with different particle groups. The correlation between mineral matters and trace elements was also studied.

## 2. RESULTS AND DISCUSSION

### 2.1. Composition and Calorific Value of Fine Slag

To study the component of Texaco gasification fine slag, proximate analysis and elemental analysis on different particle size fine slag, total fine slag, coarse slag, and raw coal were conducted (as shown in Table 1). There is still a large amount of unconverted carbon in fine slag. The carbon content of total fine slag (Cd 30%) was higher than the carbon content of coarse slag (Cd 2.15%), and approximately half the carbon content of raw coal (Cd 69.6%). The direct utilization of fine slag as a reusing fuel will affect the operating efficiency of the equipment, or direct landfill disposal also results in the waste of organic matter. However, the mineral and organic matters were not balanced in different sections of fine slag. The significant difference for carbon content was detected between the 0.125 and 0.5 mm fine slag (about Cd 40%) and the other section fine slag (Cd 13–24%). The yield of low-ash fine slag (0.3–0.5 and 1.25 mm fine slag) in the total fine slag can reach 46% (as shown in Figure 2).

![Figure 2. Screening yield and ash content of each size range.](https://dx.doi.org/10.1021/acsomega.Ja04126

In order to study the availability of graded fine slag, the bomb caloric value of raw coal and different particle size ranges were tested, as showed in Figure 3. The test results were compared with GB/T 7562-2018 (quality requirements for pulverized coal used in power generation in China). The minimum calorific value standard for power generation fuel is 12,540 J/g. The calorific value of the 0.3–0.5 mm fine slag can

| Table 1. Proximate and Ultimate Analyses of the Raw Coal and the Different Gasification Residue (%) |
|-----------------------------------------------|
| sample type | N_d (%) | C_d (%) | H_d (%) | S_d (%) | O_d (%) | A_d (%) | V_d (%) | M_d (%) | FC_d (%) |
|-------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| +0.5 mm     | 0.33    | 23.69   | 0.44    | 0.31    | 2.76    | 72.46   | 7.43    | 1.85    | 20.11   |
| 0.3–0.5 mm  | 0.41    | 45.55   | 0.88    | 0.25    | 4.26    | 48.65   | 12.15   | 5.57    | 39.19   |
| 0.125–0.3 mm| 0.31    | 35.51   | 0.97    | 0.22    | 9.90    | 53.09   | 12.31   | 6.05    | 34.60   |
| 0.074–0.125 mm| 0.17  | 17.21   | 0.56    | 0.16    | 6.47    | 75.43   | 7.28    | 1.86    | 17.29   |
| 0.045–0.074 mm| 0.17  | 14.32   | 0.42    | 0.13    | 4.69    | 80.26   | 6.29    | 1.32    | 13.46   |
| −0.045 mm   | 0.18    | 13.42   | 0.38    | 0.12    | 3.55    | 82.35   | 6.49    | 1.46    | 11.16   |
| fine slag   | 0.29    | 30.00   | 0.47    | 0.14    | 4.01    | 65.09   | 7.79    | 2.35    | 27.12   |
| coarse slag | 0.10    | 2.15    | 0.04    | 0.08    | 0.09    | 97.54   | 1.32    | 0.10    | 1.13    |
| raw coal    | 0.94    | 69.60   | 4.66    | 0.52    | 12.40   | 11.87   | 38.62   | 2.66    | 49.50   |
meet the minimum standard, and the 0.125−0.3 mm fine slag quite approximated this standard. Compared with raw fine slag, the graded low-ash fine slag has a higher value for fuel. The +0.5 mm high-ash fine slag can be used as a landfill, which is not easy to cause dust particles. In addition, the −0.125 mm high-ash fine slag can be used for building materials.

The main reason for the nonuniform distribution of organic matter with particle sizes may be due to the coal water slurry (CWS) feeding method for Texaco gasifiers. In order to improve CWS concentration, coal particles of different sizes are mixed to fill gaps. The feed coal of the Texaco gasifier is shown in Table 2. Raw coal with particle size greater than 0.5 mm accounted for 5%, and these large particles may have a shorter residence time in the gasifier. In other words, during gasification processing, the coal of different particle sizes may have different trajectories and experience different temperature ranges. Pan et al. also put forward a similar conclusion that the reaction temperature and reaction rate are determined by the action of metal oxides. However, compared with the dry powder feed gasifier, the particle size distribution of CWS served the pulp concentration. The particle size range of CWS feed was wider than that of the dry powder feed. Therefore, the size of feeding particles may be one of the main reasons for the compositional differences of Texaco fine slag. The influence of coal particle size composition on the carbon distribution in fine slag should be under further investigation.

### 2.2. XRF and XRD Analysis of Mineral Matters in Fine Slag

Ashing samples of different size range fine slag had obvious macroscopic differences (as shown in Figure 4). It implied that the elements and compositions of fine slag minerals with different particle size ranges may be different. The mineral compositions of ash samples were characterized by X-ray fluorescence (XRF) and X-ray diffraction (XRD).

The major element content (Si, Al, Ca, Fe, Na, Mg, K, Ti, S, Mn, and P) for ash samples of fine slag was measured by XRF (as shown in Table 3). The results showed that elements Si, Al, Ca, and Fe dominated the ash composition in every size range fine slag and total fine slag. Furthermore, the major element in the 0.3−0.5 and 0.125−0.3 mm fine slag is lower than the other size range fine slag and the whole fine slag. However, the main reasons are due to the lower total mineral content of these two size ranges fine slag. If the mineral oxides were taken as a whole, the ash samples in each particle size range were similar in elemental composition.

In order to maintain mineral crystal structures, low-temperature ash treatment was carried out on the gasification slag of different sizes. The crystal structures and semi-quantitative analysis of the ash samples were characterized by XRD (as shown in Figure 5 and Table 4). XRD analysis revealed that the main components were quartz, augite, and feldspar. Mineral types of different size range fine slag were the same but the content had the regular variations with the change of particle size ranges. The content of augite decreased with the reduction of size ranges. The maximum proportion of augite in the +0.5 mm fine slag reached 46.64%. Feldspar tended to be formed in small particle (<0.074 mm) fine slag and its percentage was about 70%. The highest quartz content (around 25%) was concentrated in the 0.125−0.5 mm fine slag. It can be seen that the particle size range of high-carbon particles and high quartz particles are consistent. The main reasons may be due to the short residence time and the low-temperature range of high-carbon particles in the gasifier, which is not adequate for quartz in coal to react completely with other mineral matters.

The XRD results of minerals were consistent with the macroscopic characteristics of samples in Figure 4. The physical color of feldspar with frame structure is meat red, the color of β-SiO₂ is ivory-white, and the color of the augite mineral with chain structure is varied by the action of metal cations that connect the silica tetrahedron. As the particle size decreased, the meat red color of the ash particles gradually deepened. In particular, it is difficult to find particles of other colors in 0.045−0.074 and −0.045 mm ashing particles, which also confirmed the dominant position of feldspar in small-size fine slag. In the 0.3−0.5 and 0.125−0.3 mm fine slag, many ivory-white particles can be found, which was consistent with XRD results. A variety of colored particles appeared in the gray

### Table 2. Particle Size Distribution of CWS

| particle size distribution of CWS | wt % |
|---------------------------------|------|
| <8 mesh (2.36 mm)               | 100  |
| <14 mesh (1.43 mm)              | 99.1 |
| <35 mesh (0.5 mm)               | 95.08|
| <120 mesh (0.125 mm)            | 52.33|
| <200 mesh (0.074 mm)            | 43.30|
| <325 mesh (0.045 mm)            | 32.46|

Figure 3. Calorific value of raw coal and gasification fine slag of different particle sizes.

Figure 4. Ash samples of Texaco gasification slag after screening.
samples larger than 0.5 mm, which indicated that there were many metal cations mixed in the crystal structure of augite. Quartz, calcite, and kaolinite were the major minerals in raw coal (as shown in Figure 6). At the high temperature and high pressure in the gasifier, these minerals are easy to react to form silicoaluminate with igneous rock type. Silicon dioxide can be reacted with other minerals such as Al₂O₃, Ca-containing species to form a melting state silicate. However, the temperature distribution in the gasifier is not uniform, the temperature in the center of the gasifier can reach about 2000 °C, and the temperature at the edge may only be 1100−1300 °C. Shorter residence time and lower temperatures are not sufficient for the adequate reaction of quartz. However, even at the edges of the gasification conditions, calcite- and kaolinite-containing Ca and Fe were sufficient to form melted liquid and to react adequately. It has been confirmed by XRD analysis that the characteristic peaks of calcite and kaolinite were not detected in fine slag and coarse slag. The melting and reaction of quartz may require the particles to stay in the gasifier longer and to experience higher-temperature ranges. During coal gasification, most of the minerals existed in the form of melting and a small amount of quartz was inherited from the feed coal. When the slag was cooled to a certain temperature, the homogeneous melt would precipitate crystals, but the heterogeneous melt would remain as glasses after cooling. The effective information of glasses was not obtained by XRD analysis. Therefore, mineral elements in glasses were characterized by cold field emission scanning electron microscope equipped with energy-dispersive spectroscopy (CFESEM-EDS) analysis.

2.3. CFESEM-EDS Analysis of Fine Slag. Because the amorphous structure was difficult to be characterized effectively by XRD, the CFESEM-EDS analysis was used to distinguish the surface morphology and organic and mineral matter structure composition of the fine slag (as shown in Figure 7).

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c04126)

**Figure 5.** XRD analysis of fine slag with different size ranges.

![Figure 6](https://dx.doi.org/10.1021/acsomega.0c04126)

**Figure 6.** XRD analyses of the whole fine slag, coarse slag and raw coal.

### Table 3. Major Elemental Analyses of the Total Gasification Fine Slag and Graded Fine Slag (%)*

| oxide type | +0.5 (mm) | 0.3−0.5 (mm) | 0.125−0.3 (mm) | 0.074−0.125 (mm) | 0.045−0.074 (mm) | <0.045 (mm) | raw fine slag (total) |
|------------|-----------|--------------|----------------|------------------|-----------------|-------------|---------------------|
| SiO₂       | 33.319    | 22.115       | 24.600         | 36.248           | 39.160          | 39.617      | 30.643              |
| Al₂O₃      | 13.530    | 9.716        | 10.555         | 15.393           | 17.101          | 17.525      | 13.620              |
| CaO        | 10.769    | 5.434        | 5.484          | 8.455            | 8.313           | 8.431       | 7.055               |
| Fe₂O₃      | 8.213     | 4.891        | 5.167          | 7.975            | 7.977           | 8.370       | 6.926               |
| Na₂O       | 1.666     | 1.169        | 1.213          | 2.034            | 2.302           | 2.593       | 1.780               |
| MgO        | 1.432     | 0.933        | 0.991          | 1.498            | 1.576           | 1.640       | 1.298               |
| K₂O        | 0.883     | 0.653        | 0.703          | 1.003            | 1.237           | 1.301       | 0.936               |
| TiO₂       | 0.654     | 0.453        | 0.523          | 0.684            | 0.828           | 0.945       | 0.614               |
| SO₃        | 0.327     | 0.330        | 0.368          | 0.368            | 0.297           | 0.312       | 0.332               |
| MnO        | 0.182     | 0.156        | 0.169          | 0.222            | 0.263           | 0.283       | 0.217               |
| P₂O₅       | 0.145     | 0.092        | 0.105          | 0.143            | 0.140           | 0.131       | 0.139               |

*The presented data of oxide contents were the product of the measured XRF and the ash content.

### Table 4. Semiquantitative Analysis of Different Size Ranges Based on XRD Spectra and K Value (%)

| particle size range (mm) | mineral type | >0.5 | 0.3−0.5 | 0.125−0.3 | 0.074−0.125 | 0.045−0.074 | <0.045 |
|--------------------------|--------------|------|---------|-----------|-------------|-------------|--------|
| >0.5                     | augite       | 46.64| 34.32   | 32.41     | 27.36       | 16.17       | 22.84  |
| 0.3−0.5                  | feldspar     | 48.02| 41.73   | 41.78     | 56.55       | 74.61       | 65.46  |
| 0.125−0.3                | quartz       | 5.34 | 24.03   | 25.81     | 16.09       | 9.22        | 11.70  |
| 0.074−0.125              |              |      |         |           |             |             |        |
| 0.045−0.074              |              |      |         |           |             |             |        |
| <0.045                   |              |      |         |           |             |             |        |

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2.3.1. Carbon Distribution in Different Size Range Fine Slags. Figure 7A3−F3 shows the carbon mapping areas of the 0.3−0.5 and 0.125−0.3 mm fine slag-surmounted other size ranges, which was consistent with proximate analysis and elemental analysis result. Moreover, the carbon distribution was concentrated in the field of view. The carbon distribution of the +0.5 mm fine slag was also concentrated. However, for fine slag less than 0.125 mm, the distribution of carbon was dispersed and the carbon mapping area was lower than other size range fine slag. This indicated that extracting carbon from the −0.125 mm fine slag was difficult by physical methods and not cost-effective.

2.3.2. Morphology of Minerals and Distribution of Constitution Element in Different Fine Slags. In the term of mineral components, the EDS analyses revealed that the principal elements of the fine slag included silicon, aluminum, calcium, and oxygen. The results were consistent with XRD spectra retrieval. Mineral matters in gasification slag can be divided into crystalline and amorphous glasses. Amorphous minerals were present in the shape of spherical glassy particles in gasification fine slag.3 The interesting finding is the regular changes of glassy particles in particle size ranges of fine slag (as shown in Figure 7A1−F1). In the +0.5 mm fine slag, the glassy particles were hardly found, and most minerals had the crystalline structure. In high-carbon fine slag of 0.3−0.5 and 0.125−0.3 mm, only a few glassy matrices were found. The amount of glassy matrix in the 0.074−0.125 mm fine slag was similar to that of the 0.125−0.5 mm fine slag. However, the...
0.045–0.074 and −0.045 mm fine slag had more numerous and larger size of the glassy matrix. As shown in Figure 7B1,E1, under the electron microscope, the maximum radius of glassy particles in the 0.3–0.5 mm fine slag was 2.6 μm and in the 0.045–0.074 mm fine slag was 5.3 μm. These results suggest that graded fine slag has differences in the amount and size of the glassy matrix. Fine slag with high carbon size ranges have fewer glasses and more crystals, while high-ash size ranges are the glassy matrix. Fine slag with high carbon size ranges have opposite. The size and number of glassy particles also proved the different temperature range and residence time of graded size slag.

2.3.3. Mixture Particles of Different Size Range Fine Slags. Combining the mapping of carbon and mineral elements, the overlapping phenomena between carbon and mineral elements was found. According to the scanning electron microscopy (SEM) morphology, this result was attributable to the mineral adsorption on the surface of high-carbon particles, or the mixing of carbon and other elements. Fine slag with different size ranges had a different extent of adsorption and mixing phenomena. It was hardly found in the +0.125 mm fine slag that carbon was mixed with other mineral elements. Partial minerals only stuck to the surface of high-carbon particles. However, the −0.125 mm graded fine slag existed many carbon elements mixed with other mineral elements (as shown in Figure 8). In other words, the mineral matters were dominant and carbon was embedded in mixed particles. The adhesion phenomena also existed in the −0.125 mm fine slag. It was difficult to separate unconverted carbon from less than the 0.125 mm fine slag. On the one hand, the carbon in mixture particles is encased by minerals, whose embedded feature is thin. On the other hand, it is likely that the carbon has been reacted with silicon to form silicon carbide during the gasification process.

2.4. Distribution Character of Trace Elements. In order to study the potential impacts for the environment of reusing gasification fine slag, the total concentration of several toxic elements (Cr, Cd, V, Mo, Pb, Mn, and Ni) of raw coal and gasification slag have been measured by inductively coupled plasma–mass spectrometry (ICP–MS) (as shown in Table 5). It was observed that the concentration of all measured trace elements except Mn in gasification slag was higher than that in raw coal. Especially for elements Cr, Ni, Pb, Mo, and V, the content in coarse slag and fine slag was far higher than that in raw coal. It may be due to the low content of Cd in raw coal that the enrichment between gasification slag and raw coal was not obvious. This suggested that the trace elements were inclined to be concentrated in slag than in syngas, which was consistent with other relevant research studies.

Part trace elements between coarse slag and fine slag were distinct. The content of Mn and Pb in fine slag was significantly higher than in coarse slag. Respectively, the content of Mn and Pb in fine slag was up to 684.67 and 139.24 μg/g whereas only 3.8 and 18.55 μg/g in coarse slag. Likewise, the V and Cr content of fine slag surpassed that of coarse slag, but the distinction in Cr and V was not as obvious as in Mn and Pb. For the content of Ni, Cd, and Mo, coarse slag and fine slag were rarely different. The main reason for the high concentration of Pb in fine slag may be the high pore structure of fine slag. The high-carbon particles in fine slag have high pore structure while those in coarse slag were mainly composed of spherical glasses that were bound to each other (as shown in Figure 9). Pb condensation mainly occurred in the subsequent cooling process, so it tended to combine with high-carbon particles with a high specific surface area. The Mn enrichment tendency between coarse and fine slag needs to be further studied. In general, the total trace elements contained in fine slag are higher than those in coarse slag. The potential hazard of trace elements must be considered for the reuse of fine slag.

2.4.1. Correlation Analysis between Ash Content and Trace Elements in Fine Slags. It is mentioned in Section 3.2 that mineral matters had different enrichment in graded fine slag with different particle size ranges. The trace element content also had differences in different section fine slag (as shown in Table 5). We considered that the differential enrichment of trace element content may be related to the mineral matters in fine slag. The correlation between ash content and several trace element contents of different particle sizes was studied (Figure 10). Pearson correlation coefficient (r) was used to represent the correlation between the two data sets. The correlation between mineral matters and trace elements can be calculated as follows

\[
r = \frac{n\sum_{i=1}^{n} X_i Y_i - \sum_{i=1}^{n} X_i \sum_{i=1}^{n} Y_i}{\sqrt{n\sum_{i=1}^{n} X_i^2 - (\sum_{i=1}^{n} X_i)^2} \sqrt{n\sum_{i=1}^{n} Y_i^2 - (\sum_{i=1}^{n} Y_i)^2}}
\]

Table 5. Content of Trace Elements in Gasification Fine Slag of Different Size Ranges (μg/g)

| sample type     | Cr    | Mn    | Ni    | V     | Cd    | Mo    | Pb    |
|-----------------|-------|-------|-------|-------|-------|-------|-------|
| >0.5            | 246.25| 880.57| 47.33 | 108.75| 0.19  | 6.49  | 22.36 |
| 0.3–0.5         | 93.85 | 488.97| 37.05 | 83.33 | 0.63  | 7.45  | 81.95 |
| 0.125–0.3       | 124.69| 701.31| 56.25 | 119.81| 0.75  | 10.53 | 117.67|
| 0.074–0.125     | 137.27| 907.85| 56.62 | 129.21| 0.77  | 8.75  | 109.97|
| 0.045–0.074     | 202.49| 1096.15| 77.32 | 196.04| 2.67  | 12.67 | 89.80 |
| <0.045          | 184.37| 1006.76| 78.17 | 193.69| 0.97  | 11.97 | 177.44|
| fine slag       | 140.11| 684.67| 60.56 | 142.06| 0.83  | 10.86 | 139.24|
| coarse slag     | 281.61| 3.81  | 70.18 | 197.87| 1.05  | 7.05  | 18.55 |
| raw coal        | 11.83 | 136.45| 6.69  | 13.67 | 0.09  | 0.74  | 5.85  |

Figure 8. Schematic illustration of mixture particle.
Here, $r$ denotes the correlation coefficient of trace elements and mineral matters. $n$ denotes the fine slag sample of different particle size ranges. $X_i$ denotes the content of ash or a kind of mineral component. $Y_i$ denotes the trace element content. The correlation between trace elements and minerals was classified into three grades: strong correlation, medium correlation, and weak correlation. $|r| > 0.7$ was a strong correlation, $0.7 \geq |r| > 0.5$ was a medium correlation, and $0.5 \geq |r| > 0$ was a weak correlation.

The results revealed that measured trace elements were positively correlated with minerals in fine slag. This indicated that with the increase of mineral content in fine slag, the trace element content would also increase. The level fluctuation of the $r$ value reflected that different trace elements have a distinct degree of correlation with minerals in fine slag. Chromium, manganese, nickel, and vanadium have a strong correlation with mineral matters in fine slag. Cadmium and molybdenum were at the edge of medium correlation and weak correlation; the correlation of element Pb with minerals was weak. In the high-temperature reduction atmosphere, according to thermodynamic simulation, the oxides and elemental forms of trace elements are the main forms of these metals during gasification. For instance, during gasification, $\text{Cr}_2\text{O}_3(s)$, $\text{MnO}(s)$, $\text{NiO}(s)$, $\text{NiO}(s)$, $\text{V}_2\text{O}_5(s)$, $\text{Cd}_2\text{S}(g)$, $\text{CdS}(g)$, $\text{Mo}_2\text{O}_3(s)$, $\text{PbS}(g)$, and $\text{Pb}(g)$ are the stable existing form of several trace elements.25−29

We found that trace elements in solid form are strongly correlated with minerals. In most cases, strongly correlated trace elements exist in the form of oxidation states and are bound to minerals in fine slag. For example: when the temperature exceeds 925 °C, manganese can combine with silicoaluminate minerals to form Mn-cordierite melts ($\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) according to a thermodynamic simulation of Bunt;27 $\text{V}_2\text{O}_5$ probably associated with silicoaluminate minerals according to Goodarzi.30 It can be seen from the trace element form given in the above paragraph that the part of trace elements (Cd, Mo, and Pb) was presented in the gas phase. The vaporization temperature of these trace elements and compounds was usually lower than the gasification temperature. These trace elements were called low boiling metals. Because of the low boiling points of elements Pb, Cd, and Mo, their solid-phase formation occurs mostly during the cooling and washing of syngas. Compared with high boiling point trace elements, they do not combine effectively with...
minerals in coal during gasification. Element Pb has multiple occurring states during gasification, but the elemental and sulfide form of them are dominant. Combined with Figure 10, element Pb had a weak correlation with minerals in fine slag. It has been shown in the literature that Pb and its compounds in the gas phase were condensed when the temperature is lower than 400 °C. The fixation of Pb in fine slag was most likely concentrated in cooling technology, and Pb in fine slag probably existed in physisorption. The particles with the developed microporous structure in fine slag can collect condensational Pb. Therefore, the correlation between element Pb and mineral matters was weak. Elements Cd and Mo had a near-medium correlation with mineral matters and they were also low boiling point trace elements. However, oxides had a certain percentage in their forms in the gasification reaction. Element Cd has a greater diversity of forms, which contains elemental oxides and sulfides, chlorides, and hydroxides. According to the thermodynamic simulation of J. Liu, CdO can form binary oxides with SiO$_2$ and Al$_2$O$_3$ in higher temperatures. For molybdenum, Mo$_2$O$_3$ was the main form of element Mo in the gasification reaction. When the temperature was higher than 1025 °C, Mo$_2$O$_3$ would evaporate completely, according to the study of Bunt. Therefore, the fact that partial forms of element Cd and Mo were presented as oxides and their vaporization temperature were all lower than the gasification temperature are the main reasons why the correlation between element Cr or Mo and ash content was stronger than Pb. Still, it was on the edge of weak correlation and medium correlation. Elements Cr, Mn, Ni, and V had high vaporization temperature and occur in the form of oxides. Therefore, they were a strong correlation with mineral matters. In a word, modes of occurrence and vaporization temperature caused the correlation between trace elements and mineral matters were different. Furthermore, the high evaporation temperature trace elements were mainly in the form of solid oxide during gasification. Minerals in fine slag are selectively distributed in fine slag of different particle sizes, so trace element content such as Cr, Mn, and V, which showed strong correlation with mineral matters, also fluctuated with the change of particle size ranges of fine slag.

2.4.2. Correlation Analysis of Constituent Minerals and Trace Elements in Fine Slag. In order to further study the connection between different mineral compositions and trace elements in gasification fine slag, we analyzed the correlation between different mineral compositions and trace element contents (as shown in Figure 11). Feldspar, augite, and quartz are the main minerals in fine slag, which were achieved in XRD analysis (Figure 5). The results showed that Mn, Ni, and V had a strong correlation with feldspar but they had a weak correlation with augite, and the correlation between quartz and these trace elements was negative. Mn, Ni, and V were mainly in the form of solid oxide with high vaporization temperature and had a strong correlation with total mineral matters, which were mentioned in Section 2.4.1. This suggested that the strong correlation between the elements Mn, Ni, or V and mineral matters originated from feldspar. Compared with the other six elements, chromium is a special element. It also had a strong correlation with total mineral matters and a high vaporization temperature. However, it was not strongly related to feldspar and more related to augite than other minerals. The combination with augite minerals was also shown in the +0.5 mm ash sample of Figure 4. Because Cr probably served as the...
3. MATERIALS AND METHODS

3.1. Gasification Slag Sample. Gasification fine slag, coarse slag, and raw coal were collected from the Texaco gasification unit in Shaanxi, China. The origin of feedstock is Shenfu Coalfield in the northern Shaanxi province, China.

3.2. Preparation of Grading Gasification Fine Slag. After filtration treatment, the dewatered cake still contains a large amount of moisture, so the fine slag needs further drying treatment. Fine slag was dried in a blast-drying oven at 105 °C for 3 h to a constant weight for subsequent chemical composition analysis and grading processing. Next, the dried filter cake was fully pulverized in the mortar. The treatment of mortar can completely separate the adhesive particles, but it does not affect the particle size distribution of the fine slag. Finally, the gasification fine slag was screened by the linear vibrating screen. The sieve pore sizes were 0.5, 0.3, 0.125, 0.074, and 0.045 mm. The total fine slag was divided into six sections with different size ranges. The feeding was 500 ± 10 g for each screening, the screening time was 6 min, and the process was repeated 10 times.

3.3. Analytical Methods. Proximate analysis was performed on total fine slag, graded fine slag, coarse slag, and raw coal following the Chinese standard GB/T 212-2008. An elemental analyzer was used to determine the mass percentages of C, H, O, N, and S in samples. The CFESEM-EDS (Hitachi, Japan) was used to observe the morphology and determine the surface element distribution of fine slag samples with different particle sizes. The test parameters of high voltage (15 kV) and low magnification (3000 times) were employed to obtain a better distribution diagram of the element. Major mineral elements in the different types of fine slag after high-temperature ashing were analyzed by XRF (PANalytical B.V., Netherlands). The mineral types of low-temperature ashing samples were detected by XRD (Empyrean, Netherlands). The XRD spectra were analyzed by Jade 6.5 and the integral intensity of the maximum characteristic peak of minerals was obtained. The integrated strength was combined with the RIR of different minerals given by ICCD to obtain a semi-quantitative analysis of different minerals.

3.4. Digestion Experiment. Dried samples (0.1 ± 0.001 g) were placed into the digestion tube. HNO\textsubscript{3}(aq) (5 mL of 65 wt %) and then 3 mL of 30 wt % H\textsubscript{2}O\textsubscript{2}(aq) were placed in the digestion tubes to dissolve the organic matter and part mineral matters of samples. In order to avoid the contamination of trace elements in the reagents, the purity of the reagents is guaranteed reagents and the blank tests were also carried out. After standing for 30 min, the digestion tubes were put into a microwave digestion system (manufactured by CEM Corporation, USA) for the first digestion experiment. The digestion time was 3 h and the microwave power is 1600 W. After that, 3 mL of 40 wt % HF\textsubscript{(aq)} was added for the second digestion experiment. The main purpose is to react with the residual minerals. The digestion of minerals requires the equipment to run multiple times until the solution is free of solids. Finally, the digestion liquids were decacidi and diluted. The ICP–MS (PerkinElmer NexION300x, USA) was used to determine the trace elements in digestion liquids. The concentrations of seven trace elements of interest, that is, Cr, Mn, V, Ni, Cd, Pb, and Mo, were examined.

4. CONCLUSIONS
Based on the classification characteristics of fine slag in Texaco gasification, this work studied the distribution of mineral matters, organic matters, and trace elements (Cr, Mn, Ni, V, Cd, Pb, and Mo). The major conclusions are as follows:

1. The composition of fine slag with different size ranges showed significant differences. The high-carbon particles are concentrated in the median section (0.125−0.5 mm), which was twice the high-ash section. The carbon distribution of the +0.125 mm fine slag was concentrated and it is possible to further extraction. However, the carbon distribution of the −0.125 mm fine slag was dispersed. The mixture particles that carbon was embedded in mineral matters are the main reasons for the difficult separation.

2. The main components of amorphous glassy particles are aluminosilicate. The amount and size of glassy particles are significant differences between the high-carbon section and the high-ash section.

3. The strong correlation between element Mn, Ni, and V and mineral matters originated from feldspar. Compared with other elements, element Cr had a stronger correlation with augite as the connecting metal ion. Although element Cd, Mo, and Pb show weak correlation with mineral matters, because of the trace elements in the form of oxides, the correlation of...
elements Cd and Mo and mineral matters was in close proximity to the edge of medium level, and element Pb was far from the edge. Element Pb was mainly enriched in the high-carbon section with the developed pore structure.

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Notes

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