The environmental characteristics of usage of coal gangue in bricking-making: A case study at Huainan, China

Chuncai Zhou a,b,c,d, Guijian Liu a,b,d,* , Shengchun Wu c, Paul Kwan Sing Lam c,d

* CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefe, Anhuii 230026, China

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HIGHLIGHTS

- Brick-making using coal gangue is one of the important coal gangue recycling utilization.
- The enrichment behaviors and health impacts of natural radionuclides during coal gangue brick making are studied.
- The emission characteristics of toxic elements from the coal gangue brick firing processes are evaluated.

ARTICLE INFO

1. Introduction

Toxic elements in atmosphere may affect humans directly (predominantly through inhalation) and indirectly through ingestion (food) (Ruhl et al., 2009). Health impacts associated with toxic elements include inflammation, altered the sensitivity of epithelia, changed immunological mechanisms, and increased cancer risk (Goldhaber, 2003; Proctor et al., 2006; Kang et al., 2011). Source identification and quantification of toxic elements are extremely significant measures which could help to control their emissions and effectively reduce the environmental (health) impacts (Mu et al., 2012). The emission behaviors of toxic elements during coal mining, transportation (Lough et al., 2005; Shafer et al., 2012), combustion (Querol et al., 1995; Singh and Paul, 2001; Yi et al., 2004), and waste disposal (Zhang et al., 2008; Gidarakos et al., 2009) are received fairly intensive studies. However, the investigations on the unintentional release and environmental impacts of toxic elements during the processes in coal mining accessory industries are extremely scarce (Yang et al., 1998; Zhang et al., 2008).

Coal gangue is the by-product of coal mining. The average production of coal gangue is approximately 10–15% of raw coal production in China, depended on mining and geological conditions (Liu and Liu, 2010). Due to the high content of clay minerals and carbon, coal gangue could also be a valuable resource. Beneficial uses of coal gangue include power generation, and as a component for construction materials, e.g. cement, brick, concrete and other places (Liu et al., 1996; Zuo, 2009).

Brick-making using coal gangue is one of the important coal wastes recycling utilization. The processes for coal gangue brick-making are consisted of crushing, screening, stirring, ageing,
molding, pressing, drying in oven, firing and testing (Kumar, 2002). The prepared coal gangue is subjected to external heating to approximately 1000 °C in an oxygen-free atmosphere during firing. During high temperature combustion of coal gangue, toxic elements contained in the coal gangue undergo complex reactions that lead to the vaporization of volatile elements as gaseous phase (Clarke, 1993), which are then released into the atmosphere. It has been reported that the emission behaviors of toxic elements during combustion depended on such factors as elemental physical and chemical properties, initial concentration and mode of occurrence. (Jak et al., 1998). However, previous studies of coal gangue brick making emissions were primarily focused on fluoride (Xie et al., 2003), and little information about the partitioning behaviors of toxic elements from brick making is available. It is thus of great interest to study the structural characteristics and behavior of elements involved in coal gangue combustion in order to understand their fates.

Moreover, during the firing of coal gangue, the materials contain the alumino-silicate minerals will later comprise the brick, most of the thorium, radium and potassium isotopes follow (Coles et al., 1978). As bricks are finally used by the construction industry, the behaviors of the natural radionuclides (226Ra, 232Th and 40K) should be investigated in order to assess their impact on human health. Extensive studies have reported that the mineralogical and chemical properties in which the radionuclides exist in coal have an important influence on their subsequent chemical reactions and enrichments characteristics in combustion (Coles et al., 1978). Therefore, the transformation characterizations of mineralogical and chemical properties during coal gangue combustion are discussed systematically in this study.

The main objectives of the present study are to determine (a) the enrichment behaviors and health impacts of natural radionuclides during coal gangue brick making and (b) the emission characterizations of toxic elements from the coal gangue brick firing processes. The outcome of this study is expected to provide a natural radionuclide and toxic element inventory for further research.

2. Experimental

2.1. Sample collection and preparation

Since composition of toxic elements and natural radionuclides in coal gangue can vary greatly between mines and even within a single coal seam, composition of combustion products from a single plant can also vary. Thus, in order to generalize the results of a limited number of tests, 10 coal seam roofs/floors or partings (50–100 kg) from the No. 11 coal seam (DJ-1, DJ-2, DJ-3, DJ-4 and DJ-5) and No. 13 coal seam (DJ-6, DJ-7, DJ-8, DJ-9 and DJ-10) were collected from Dingji Coal Mine in Huainan Coalfield. Based on the representative within a coal seam studies, the coal gangue samples were taken by cutting channels downwards. After collection, the samples were immediately stored and sealed in a plastic bag to prevent contamination. To obtain representative samples, the samples were air-dried and crushed prior to pass through a 2 mm mesh sieve in order to homogenize them for the subsequent analysis.

2.2. Combustion procedure

In general, the combustion temperature in coal gangue brickfield is 900–1000 °C (Raut et al., 2011). Accordingly, coal gangue samples (100 g each) were fired in an electric oven in porcelain crucibles and in an oxidizing atmosphere at 800 °C maintained for 1 h followed by 1000 °C for another hour (Raul et al., 2011). After combustion, the samples were cooled down to room temperature in a dryer. The combustion slag was crushed so that it could pass through a 2 mm mesh sieve in order to homogenize it for the subsequent analysis.

2.3. Radioactivity analysis

The powder coal gangue samples and combustion products (slag) were homogenized and dried in a temperature controlled furnace at 100 °C for 24 h to remove moisture. After cooling, the dry materials (150 g) were then sealed in gas-light, radon impermeable cylindrical (diameter of 40 mm) polyethylene containers. The samples were sealed for 30 d to reach radioactive equilibrium. A GEM60P4-83 high-purity germanium gamma ray spectrometer was employed to determine the concentrations of 222Rn, 226Ra and 40K. The activities of 228Ac and 209Tl in equilibrium with their parents are applied to represent the 222Rn activity, while the activities of 214Pb and 214Bi are applied to represent the 226Ra activity. The gamma lines used for the qualification of the radionuclides are according to the methods reported by Cevik et al. (2008).

2.4. Trace element analysis

The coal gangue and combustion product (slag) samples were digested using an acid mixture (HCl:HNO3:H2O) ratio of 3:3:2 in a microwave oven. After digestion, the concentrations of toxic elements in coal gangue and combustion product (slag) samples were determined by inductively coupled plasma mass spectrometry (ICP-MS). The accuracy of most of the toxic elements was corrected by standard reference material NIST 1632b (coal) and the remainder of the elements by GBW07406 (GSS-6) (soil). The acceptable precision is within ±5% for the toxic elements. If the difference between the calibrated values and the standards is more than 5%, the apparatus needed to recalibrate.

In addition, the sequential extraction experiment was also employed to provide information about the modes of occurrence of toxic elements in coal gangue (Tessier et al., 1979). Samples were subjected to specific solvents in five-step sequential extraction procedure, the modes of occurrences of trace elements are classified into five fractions: exchangeable, carbonate-bound, Fe-Mn oxides bound, organic matter bound, residual. The fractions acquired after each extraction step were analyzed for As, Cd, Cu, Cr, Mn, Ni, and Zn by inductively coupled plasma mass spectrometry (ICP-MS).

In order to guarantee the precision and accuracy of the experimental data, all the experiments for each sample were repeated three times.

3. Results and discussion

3.1. The properties of coal gangue

The main chemical compositions (Table 1) of coal gangue are SiO2 (54–60%), Al2O3 (23–27%), Fe2O3 (6–9%) and CaO (7–11%), which are deemed a suitable raw material for brick making (Raut et al., 2011). The high SiO2 and Al2O3 contents in the coal gangue suggested high compositions of clay minerals and quartz. The high concentration of Fe2O3 is predominantly controlled by sulfide minerals (i.e., pyrite) and carbonate minerals (i.e., siderite). The CaO content in coal gangue is mostly associated with carbonate minerals (i.e., calcite). Traces of other components such as K2O, Na2O, MgO, TiO2 are also identified and are less than 2%. The morphological characterizations of coal gangue and combustion product (slag) are presented in Fig. 1. The coal gangue particles (Fig. 1a), with a diameter of 5.0 μm are thin sheet in shape. After
3.2. The behavior of natural radionuclides during combustion

The radioactivity concentrations of these radionuclides in coal gangue and combustion products are presented in Table 2. The mean specific activity concentrations of radionuclides $^{226}$Ra, $^{232}$Th and $^{40}$K are 44, 88 and 527 Bq kg$^{-1}$ in coal gangue, respectively. The concentration of $^{40}$K accounted for approximately 84–90% of the total gamma activity of the coal gangue which indicated that $^{40}$K is the largest contributor to the total activity for the coal gangue.

For comparison, the activity concentrations of these radionuclides in coal and coal gangue from Anhui Province, China and other countries are shown in Table 2. According to Table 2, the activity concentrations of $^{232}$Th and $^{40}$K in Dingji Mine are much higher than the corresponding concentrations in Anhui coal, Anhui coal gangue, China coal, China coal gangue (Liu et al., 2007), Poland coal and Indian coal (Bem et al., 2002; Mishra, 2004), show an indication that the activity concentrations of these radionuclides are high.

The coal gangue composition has an extremely significant contribution on the radionuclides enrichment factors. Enrichment factors relative to the coal gangue are calculated for the radionuclide concentrations observed. The enrichment factor (EF) is defined as the ratio of the content of a radionuclide (X) and $^{40}$K in the sample divided by the corresponding ratio in the coal gangue (Coles et al., 1978).

$$\text{EF} = \frac{X_{\text{slag}}/^{40}\text{K}_{\text{slag}}}{X_{\text{coal gangue}}/^{40}\text{K}_{\text{coal gangue}}}$$  (1)

This normalizes the apparent enrichment resulting from the loss of carbon or organic matter during the firing processes. $^{40}$K is used in the formula since the concentration of $^{40}$K remained more or less constant in all samples.

The mineralogical, chemical properties and modes of occurrence of radionuclides in coal gangue have an important effect on their subsequent behaviors during combustion, weathering and leaching. In coal gangue, radionuclides can be associated with both organic matter and inorganic minerals. The variations of modes of occurrence of radionuclides in coal gangue indicated different behavior during coal gangue combustion. It has been identified that radionuclides associated with organic matter and sulfides are more easily volatilized than those with affinity to silicate minerals (Coles et al., 1978). Coles et al. (1978) hypothesized that much of the alumino-silicate minerals (mostly clay) form a melt phase during combustion, and most of the Ra and Th isotopes follow. Cevik (2008) determined the activity concentration of radionuclides in Turkey coal and corresponding slag, found that the activity concentration of $^{226}$Ra in slag is two times higher than the concentration in coal. Moreover, the activity concentration of $^{226}$Ra in Indian coal and slag are also found to follow the same trend (Mishra, 2004; Cevik et al., 2008). The correlation analysis
The activity concentration of $^{226}$Ra have a positive correlation ($\tau = 0.6534$) with ash yield indicating an inorganic affinity. The activity of $^{226}$Ra in combustion product (slag) is much higher than the corresponding concentration in coal gangue, and the EF values of $^{226}$Ra is 1.08 (Table 2) which indicate that radionuclides in coal may be associated with silicate minerals. Thorium is normally associated with zircon ($\text{ZrSiO}_4$) (Kirby, 1974), which is a very chemically resistant mineral and existed in many common rocks. It is presumed that thorium observed in coal gangue is deposited as zircon contemporaneously along with the other silicate based minerals. The positive correlation ($\tau = 0.6398$) of the activity concentration of $^{226}$Ra with ash yield and the EF value of 1.13 demonstrated the inorganic affinity effectively.

Since brick is an important material for the construction industry, the potential health risks should be carefully considered. To assess the radiological hazards, the radium equivalent activity ($R_{aeq}$) and external hazard index ($H_{ex}$) of the coal gangue combustion products are used in the study. Meanwhile, the air absorbed dose rates and annual effective dose are also calculated to evaluate the environment impacts.

It is hypothesized that 370 Bq kg$^{-1}$$^{226}$Ra or 259 Bq kg$^{-1}$$^{232}$Th or 4810 Bq kg$^{-1}$$^{40}$K produce the same gamma dose rate (Mishra, 2004; Cevik et al., 2008). Therefore, the radium equivalent activity and external hazard index can be calculated according to Beretka and Mathew (1985) as:

$$R_{aeq} = C_{Ra} + 1.43C_{Th} + 0.07C_{K}$$

(2)

$$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_{K}/4810 \leq 1$$

(3)

where $C_{Ra}$, $C_{Th}$ and $C_{K}$ are the activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K in Becquerel per kilogram, respectively. The maximum value of $R_{aeq}$ in construction materials must be less than 370 Bq kg$^{-1}$ for safe use (OECD, 1979), and the maximum value of $H_{ex}$ equal to unity corresponds to the limit of $R_{aeq}$ (Bq kg$^{-1}$). The calculated values of $R_{aeq}$ in combustion slag ranged from 236.8 to 398.9 Bq kg$^{-1}$ (Table 3) with an average of 345.2 Bq kg$^{-1}$, which is near the recommended limit of 370 Bq kg$^{-1}$. The calculated values of $H_{ex}$ ranged from 0.64 to 1.18 with an average of 0.89, which is also near unity. The average relative contributions to $R_{aeq}$ and $H_{ex}$ due to $^{226}$Ra, $^{232}$Th and $^{40}$K are 17%, 66% and 17% in combustion slag, respectively.

Besides the radium equivalent activity ($R_{aeq}$) and external hazard index ($H_{ex}$), the total outdoor air absorbed dose rate (nGy h$^{-1}$) due to terrestrial gamma rays at 1 m above the ground is calculated from $^{226}$Ra, $^{232}$Th and $^{40}$K. The conversion factors used to calculate the absorbed dose rates are given as follows (OECD, 1979): 

$$D(\text{nGy h}^{-1}) = 0.46 C_{Ra} + 0.623 C_{Th} + 0.414 C_{K}$$

(4)

The calculated results show that the absorbed dose rates range from 108.55 to 217.63 nGy h$^{-1}$ with mean value of 148.78 nGy h$^{-1}$ in combustion product (Table 3), which are higher than the average value of global primordial radiation of 59 nGy h$^{-1}$ (UNSEAR, 2000) and the Chinese natural gamma radiation dose rate of 63.0 nGy h$^{-1}$ (UNSECR, 2000). To estimate the annual effective dose rates, the conversion coefficient from the absorbed dose in air to the effective dose (0.7 nGy h$^{-1}$) and the outdoor occupancy factor (20%) presented by UNSCEAR (2000) are used. Therefore, the effective dose rate is calculated via the following formula (OECD, 1979):

Effective dose rate ($\mu\text{Sv y}^{-1}$) = $D(\text{nGy h}^{-1}) \times 8760(\text{y}^{-1}) \times 0.7 \times 10^{6} \mu\text{Sv}/10^{8} \text{nGy} \times 0.2$

(5)

The calculated effective dose rates in air in combustion product (slag) varies from 172.47 to 206.25 $\mu\text{Sv y}^{-1}$ with an average value of 179.32 $\mu\text{Sv y}^{-1}$.

The environmental effect of natural radionuclides is considered to be negligible because the $R_{aeq}$ values and $H_{ex}$ are 345 Bq kg$^{-1}$ and 0.89, respectively, and are less than the limit values of 370 Bq kg$^{-1}$ and 1, respectively. However, since the values of $R_{aeq}$ and $H_{ex}$ are near the limit values, the environmental and health impacts should be considered noteworthy.
3.3. The emission behavior of toxic element during combustion

The most significant analysis of toxic element behavior during combustion may be obtained by calculating the mass loss of element from an especial sample. The 11 toxic element behaviors (As, Cd, Co, Cr, Cu, Mn, Ni, Se, Sn, V and Zn) during coal gangue brick firing are described and discussed in this section.

The volatilization ratio (Vr) used to evaluate the toxic elements behaviors during coal gangue combustion are defined as:

\[
V_r = \left[ 1 - \frac{\text{Concentration in slag}}{\text{Concentration in coal gangue}} \times \text{Coal gangue yield} \right] \times 100\%
\]

The concentration of coal gangue, combustion product (slag) and corresponding volatile ratio are given in Table 4. Apparently, the concentrations of toxic elements are enriched in coal gangue product (slag) when compared with the coal gangue. The volatilization ratio can reflect the toxic element effectively, and it can be explained by the loss of carbon or organic matter during the firing processes. According to the volatilization ratio, the selected toxic elements can be divided into two groups, Group A, whereby low volatile tendencies are represented by Co, Cr, Mn and V which have a volatilization ratio less than 5%, and Group B, represented by As, Cd, Cu, Ni, Se, Sn and Zn which have high volatilization ratio of more than 20%.

Manganese and vanadium exhibited generally similar tendencies (Vr < 3%) during combustion. For all of the selected samples, these elements are quantitatively retained in the slag (product). According to the sequential chemical extraction experiment, Mn and V are mainly existed in residual fraction, especially associated with aluminosilicate minerals (Finkelman, 1995; Goodarzi, 2000). It is implied that the volatilize behaviors of the toxic elements are mostly dependent on their speciation in the raw materials. A higher residual fraction may result in a lower volatilization ratio during combustion. Similarly, Co and Cr are regarded as non-volatile elements (3% < Vr < 5%) since they are mainly associated with residual fraction (83% and 92%, respectively) in the coal gangue. It is reported that Cr in coal gangue is mainly found in clays, especially due to the stability of its structure as Cr$_2$O$_3$ (Huggins and Huffman, 1996). In addition, the insignificant loss of Co in this study may also be attributed to the low content of sulfide minerals in the coal gangue, as Finkelman (1995) reported that Co is generally associated with sulphides.

The combustion of coal gangue contributed significantly to the volatilization behaviors of As, Cd, Cu, Ni, Se, Sn and Zn. The volatilization ratios of As, Cd, Cu, Ni, Se, Sn and Zn are 32.61%, 41.35%, 35.44%, 18.28%, 43.62%, 53.27% and 38.63%, respectively. Arsenic, Cu, Se and Zn are the toxic elements which have a good association with sulfide minerals, such as pyrite, copper pyrite, selenium sul-fide (SeS$_2$) and blende (ZnS) (Swaine, 1995). Base on the result of sequential chemical extraction (Fig. 3), these elements are mainly associated with Fe–Mn oxides bound, organic matter bound and carbonate bound, which are instable fractions and may lead to high volatilization ratios during combustion.

The arithmetic mean values of As, Cd, Cu, Ni, Se, Sn and Zn are 12.19, 2.42, 23.57, 30.87, 3.34, 2.45 and 30.81 mg kg$^{-1}$ in Huaian coal gangue (Table 4) (Cai et al., 2008), respectively. In general, the volatile compounds are released into the atmosphere during coal gangue brick-making. Many studies have been focused on the monitoring methodologies of the atmospheric emission inventories of toxic elements, such as predictive models (Eddinger, 2005), mass balance (Roberson, 2002; Pavlish et al., 2003; Goodarzi, 2004; Tang et al., 2007; Chen et al., 2013), wet chemistry measurements by EPA Method 101A and Method 29 (Ryan and Keeney, 2004), Sorbent traps tests (EERC, 2001), and continuous and semi-continuous tests (Smith et al., 2005). Among the aforementioned monitoring methods, mass balance is the most common method to estimate the atmospheric emission inventories. Tang et al. (2007) used mass balance to analyze mercury emission from coal combustion in Guiyang power plants, and shown that coal burning in Guiyang emitted 1898 kg Hg to the atmosphere in 2002. Chen et al. (2013) introduced a simplified mass balance method to estimate the emissions of F, As, Se, Hg, and Sb from coal combustion, and shown that the Hg emission (126.3 t) acquired by the simplified method is perfectly proximate to the inventory (124.8 t and 108.6 t) calculated by Streets et al. (2009) and UNEP 2011, respectively, indicated that the accuracy and feasibility of the simplified method. Therefore, the method introduced by Chen et al. (2013) is used to estimate the gaseous emission of toxic element from coal gangue brick firing process. The following formula is adopted to calculate the gaseous emission (E) (Chen et al., 2013):

\[
E = C_b \times CC \times V_r
\]

where E is the gaseous emission of element per year; Cb is the coal gangue consumption due to brick making per year; CC is the concentration of element in Huainan coal gangue; and Vr is the volatilization ratio of element during brick making.
to predict the flux requirements for coal ash.

As reported, more than 6 million tons of coal gangue is used to make bricks in Huanian (Cai et al., 2008). It is mean that about 23.85 t arsenic, 6.00 t cadmium, 50.11 t copper, 33.86 t nickel, 8.74 t selenium, 7.83 t stannum and 71.41 t zinc are released into the atmosphere from coal gangue brick making processes per year (Table 4). It may cause serious environmental issues if no countermeasure will be adopted.

4. Conclusions

This study has provided an initial assessment of the partition behaviors of natural radionuclides and toxic elements associated with the coal gangue brick making processes in Huanian, China. The transformation of natural radionuclides during coal gangue bricks firing indicated that these radionuclides are mainly existed in residuals. The 11 trace elements could be roughly classified into two groups according to their emission characteristic: (a) first cluster with high volatile elements (As, Cd, Cu, Ni, Se, Sn and Zn), (b) second cluster, represented (Co, Cr, Mn and V), represent the low volatilization tendencies. The study also highlighted that the behaviors of natural radionuclides and toxic elements could have a severe health impact on local communities and workers.

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References


Kirby, H.W., 1974. Geochemistry of the Naturally Occurring Radioactive Series, National Technical Information Service, p. 82.


