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RESEARCH ARTICLE

Risk assessment of human exposure to heavy metals, polycyclic aromatic hydrocarbons, and radionuclides in oil-based drilling cutting residues used for roadbed materials in Chongqing, China

Deming Xiong[1] · Chaoqiang Wang[2]

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Abstract
Oil-based drilling cutting residues (OBDCRs) contain many kinds of carcinogenic contaminants, such as heavy metal elements, polycyclic aromatic hydrocarbons (PAHs), and natural radioactive materials (NORMs), which are great risks for the environment and human health. This study investigated the chemical composition, the radioactive strength, the heavy metal contents, and the org matter contents in OBDCRs and estimated the health risks due to exposure to heavy metals, PAHs, and radionuclides in OBDCRs used for roadbed materials. From the measurements, it was found that the content values of benzopyrene (a), diphenylanthracene (a, h), and petroleum hydrocarbons exceeded the standard limit. The content values of Cu, Zn, As, and Ni were higher than 50% of the standard limit. If OBDCRs were directly used to make roadbed materials, the total carcinogenic risk values (CR_n) of As, benzoanthracene (a), benzopyrene (a), and dibenzoanthracene (a, h) were all higher than 10^{-6}. The average absorbed dose rate was higher than 80 nGy/h. There were greater risks of carcinogenic environment and potential harms to human health. To reduce the health risks, it is necessary to consider the strategy of the utilization of OBDCRs, the working time, and the service life of the recycled OBDCRs and establish a legal standard and liability for the utilization of OBDCRs as solid waste resources.

Keywords Oil-based drilling cutting residues · Roadbed materials · Heavy metals · Polycyclic aromatic hydrocarbons · Radionuclides · Risk assessment

Introduction

Oil-based drilling cuttings (OBDCs) are solid wastes produced during shale gas drilling. They are complex multiphase systems containing mineral oil, alkanes, and their derivatives, as well as a variety of heavy metals. They are mainly composed of waste oil-based drilling fluid, cuttings and sewage (such as mechanical sewage, flushing sewage, water in the rock formation), which are characterized by variability, complexity, and high toxicity. Therefore, stacking, transportation, and treatment of OBDCs may cause harm to the local ecological environment and human health (Ball et al. 2012; Soeder et al. 2014). The environmental hazards of OBDCs mainly include the following aspects: (1) affecting plant growth, due to the influence of high-concentration soluble salts; (2) polluting groundwater, surface water, and soil by organic matters and heavy metals; (3) destroying the local ecosystem and affecting the biodiversity; (4) giving radioactive hazards.

It has been proved that these polycyclic aromatic hydrocarbons (PAHs) and heavy metals in OBDCs can cause DNA damage, inflammation, lung and heart disease through ingestion, inhalation, and dermal contact. For example, naphthalene, fluorene, phenanthrene, fluoranthene, benzopyrene (a) can cause lung cancer, skin cancer, gastric cancer, etc. (Xu et al. 2016; Jones et al. 1991). They affected the reproduction of foraminifera and fish in the West Indian Ocean (Jagwani et al. 2011) and lead to the decline of species, density and amount of biomass in the Bohai Sea during 2006–2011 (Zhang et al. 2015). The heavy metals are also harmful to

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✉ Chaoqiang Wang
wcq598676239@126.com

[1] Chongqing Environmental Protection Center for Shale Gas Technology & Development, Fuling, Chongqing 408000, China

[2] School of Material Science and Engineering, Chongqing Jiaotong University, Chongqing 400074, China

human health by inducing enzyme activity (Gillis et al. 2012), destroying the central nervous system (Gillis et al. 2012; Liu et al. 2013; Chen et al. 2016), and causing headache, liver disease, cardiovascular disease, and respiratory disease (Liu et al. 2013; Lippmann et al. 2006).

Also, OBDCs contain many natural radioactive materials (NORMs), which are rocks from the stratum. If OBDCs are brought to the surface, they will affect the ecological environment and human health (Lin et al. 2019). According to the existing researches (Shen et al. 1983; Wang et al. 2019), the Longmaxi Formation shale in Sichuan Basin contains a high amount of radioactive materials, such as Ra (226), Th (232), U (238), and K (40) and the radioactivities are higher than the background values. It is worth noting that Ra (226) exists in gaseous form and can be easily inhaled into the human body. The α particles produced by the decay of Ra (226) can cause corrosion damage to the respiratory system and induce cancers. At present, the World Health Organization has classified Ra (226) as the class I carcinogen. Therefore, it is necessary to evaluate the radioactive health risk of OBDCs in the process of their utilization.

Recently, some researchers have investigated the human health risk caused by OBDCs. However, most of them focused on the impact of heavy metals in OBDCs on the environment and drilling workers (Wang et al. 2017a, b; Xu et al. 2018). Few investigated the effects of heavy metals, PAHs, and NORMs of oil-based drilling cutting residues (OBDCRs) on human health. The particle sizes of OBDCRs are very small with diameter of 1–300 μm. They are more likely to affect workers' health by ingestion, skin touch, and inhalation. So it is of great significance to understand the characteristics of OBDCRs and their human health risks.

This study investigated the chemical composition, the radioactive strength, the heavy metal contents, and the organic matter contents in OBDCRs and estimated the health risks due to exposure to heavy metals, PAHs, and radionuclides when OBDCRs were used for roadbed materials. The heavy metal contents in OBDCRs were analyzed and identified using an ICP-OES machine. The organic matter contents were analyzed by FT-IR and GC-MS. The radionuclides were analyzed by a gamma ray spectrometer. The objective of this study was to identify the characteristic pollutants and their pollution levels in OBDCRs focusing on the harm to human health (workers and inhabitants) and the environment and provide rational suggestions for the utilization of OBDCRs.

Materials and methods

Study area

The study area was the Fuling shale gas field located in Fuling District (29° 43′ N, 107° 35′ E), Chongqing, China (Fig. 1). It belongs to the karst landform. The terrain is mainly mountainous and hilly, and the ground elevation is 200–1000 m. The rivers are well developed, and streams and rivers flow continuously all over the year. The climate is a typical subtropical humid monsoon climate. There are 317 days of frost free days and 1327.5 h of sunshine. The dominant wind direction is the northeast wind, with a frequency of 54%. The annual average temperature is 18.2 °C with an average temperature of 3 °C in winter and 28 °C in summer. The rainy season is mainly distributed from May to October, and the annual rainfall is about 1200–1400 mm.

Sample collection and preparation

According to the field statistics, about 300,000 t of OBDCRs have been produced, in which 100,000 t of OBDCRs are temporarily stored. Sinopec Chongqing Fuling Shale Gas Exploration and Development Co., Ltd, is a national demonstration area for shale gas exploration and development, and the largest shale gas field in China. OBDCRs of Fuling shale gas field can represent China's OBDCRs. In this study, three OBDCR samples (YG-1 in No. 1, YG-2 in No. 2, YG-3 in No. 3, as shown in Fig. 1) were obtained from different OBDC recycling centers in the north, central, and south areas of the Fuling shale gas field. The samples were taken according to the relevant requirements of the technical specifications on sampling and sample preparation for industrial solid wastes (China 1998). During sampling, each sample was taken from one quarter of six uniformly distributed mixed samples across the OBDCR storage warehouse (Fig. 2). Then, 1 kg of each sample was collected, preserved, and transported to Chongqing Environmental Protection Engineering Technology Center for Shale Gas Development for their analysis. In this study, it was assumed that OBDCRs can be directly used for roadbed materials (100%) for paving roads and platforms. The subjects of this study are classified as adults under the China Environmental Protection Ministry (China 2014) with an age range of 18–70 years old and a bodyweight of 56.8 kg.

XRF and XRD

The elemental compositions of the OBDCR samples were characterized by the PANalytical Axios Fast XRF spectrometer. The main instruments utilized were the XRF spectrometer (PW4400), a high-frequency melting furnace (Analvmate-v4d), and a platinum crucible (Pt 95% + Au 5%). The solvent used in the experiment was a mixture of lithium tetraborate and lithium carbonate with a mass ratio of 6:1. The used anhydrous lithium bromide was a high-grade pure one. P10 was composed of methane and argon with a mass ratio of 1:9. The X-ray tube voltage was 60 kV, and the current was 60 mA.

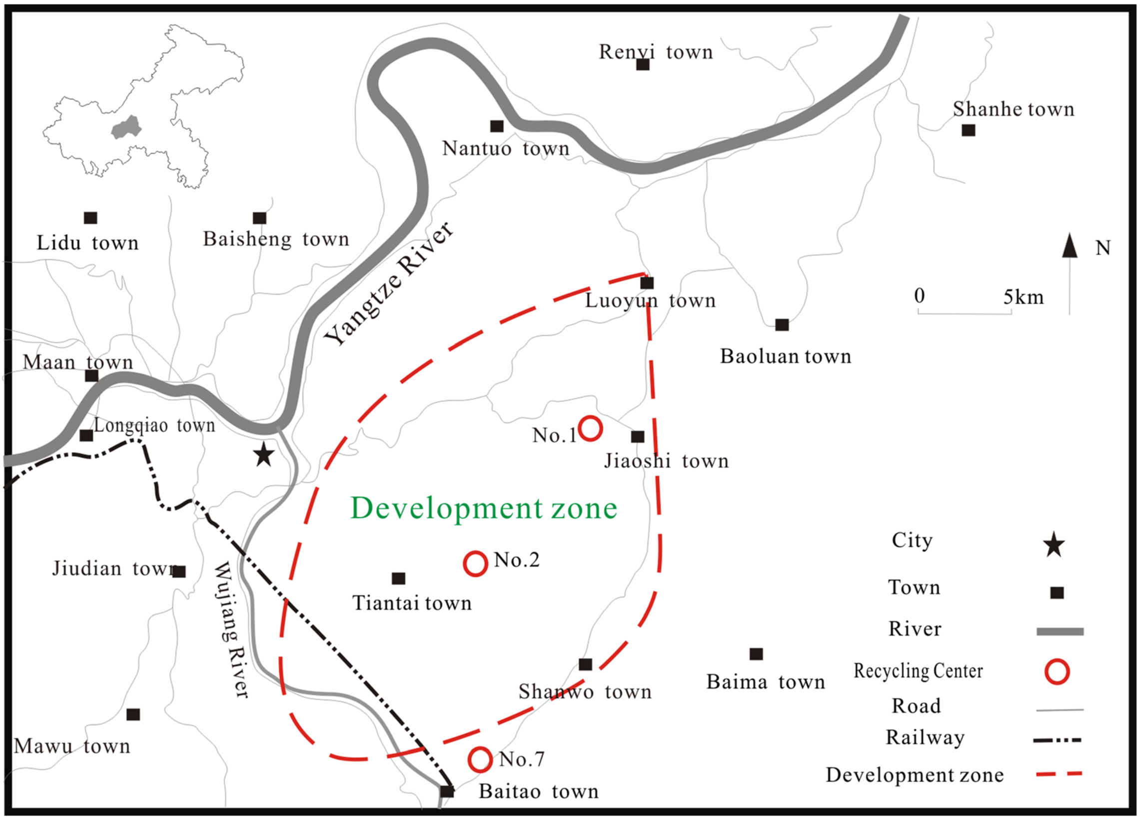


Fig. 1 Geographic location map of the Fuling shale gas field

The analytical crystals used in the test were lif200, ge111, pe002, and PX1.

The material compositions of the OBDCR samples were determined by the X-ray diffraction (XRD), analyzed with the Cu-Kα radiation operating at 35 kV and 60 mA. The 2θ ranged from 10 to 65° was scanned at 1.26°/min. The XRD spectrum was analyzed by the software of X'Pert HighScore and Plus MDI Jade 5.0.

FT-IR

The FT-IR spectroscopy was carried out by using the Spectrum One FT-IR (PE companies of the USA). After mixing with KBr, the OBDCR samples were pressed at 2000 psi/min to produce wafers for analysis. The analysis was carried out with the frequency range of 900–4000 cm^{-1} and the resolution of 0.5 cm^{-1}.

Fig. 2 Production, storage, and treatment processes of OBDCs

GC-MS

The gas chromatography-mass spectrometry (Hewlett Packard HP6890GC-HP5973MS) was used to analyze the organic components in the OBDCR samples. The chromatographic column was DB-5 (30 m × 0.25 mm), and the carrier gas was helium at the flow rate of 1 mL/min. The mass spectrometry electron energy was 70 eV, the ion source temperature was 230 °C, the injection temperature was 80 °C, and the holding time was 1 min. Then, the temperature was raised to 280 °C at 3 °C /min and kept constant at 280 °C for 20 min. The Hewlett-Packard Chemstation data system collected and processed the data measured by GC-MS.

ICP-OES

The trace element and heavy metal contents in the OBDCR samples were determined by the ICP-OES analytical instrument (PE Avio200). The test conditions were as follows. The RF power was 1200 W, the nebulizer flow rate was 0.2 L/min, the plasma flow rate was 9.0 L/min, the auxiliary gas flow rate was 0.2 L/min, the gas pressure was 357.0 kPa, the sample flow rate was 1.0 mL/min, the integration time was 1–5 s, and the reading delay was 50 s.

Gamma ray spectrometer

The analysis was carried out by using the gamma ray spectrometer (HD-2001) manufactured by Shanghai Microspectrum Chemical Technology Service Co., Ltd. The gamma ray energy spectrometer measured the gamma ray in the energy range between 40 and 2000 keV. It consisted of a NaI (TI) detector with a relative efficiency of 20%. For measuring the 1332.5 keV gamma ray emissions from ^{60}Co, the resolution was 2.5 keV.

Health risk assessment

Carcinogenic risk analysis of OBDCRs by ingestion

In non-sensitive areas, when assessing the carcinogenic effect of a single pollutant, the lifetime hazard of adult exposure should be considered only. The formula for calculating the exposure amount of OBDCRs is expressed by Eq.1(China 2014).

$$\mathrm{CR_{ois}} = \frac{\mathrm{OSIR_a} \times \mathrm{ED_a} \times \mathrm{EF_a} \times \mathrm{ABS_o}}{\mathrm{BW_a} \times \mathrm{AT_{ca}}} \times C_{\mathrm{OBDCRs}} \times \mathrm{SF_o} \times 10^{-6} \quad (1)$$

where $\mathrm{CR_{ois}}$ (unitless) is the carcinogenic risk when exposed to a single pollutant by ingestion of OBDCRs, $\mathrm{SF_o}$ (kg day/mg) is the carcinogenic slope factor of ingestion, C_{OBDCRs} (mg/kg) is the concentration of contaminants in OBDCRs, $\mathrm{OSIR_a}$ (mg/day) is the daily oral ingestion rate of OBDCRs by adults, $\mathrm{ED_a}$ (a) is the exposure duration of adults, $\mathrm{EF_a}$ (d/a) is the exposure frequency of adults, $\mathrm{ABS_o}$ (unitless) is the absorption efficiency of oral ingestion, $\mathrm{BW_a}$ (kg) is the average body weight of adults, and $\mathrm{AT_{ca}}$ (day) is the average time for the carcinogenic effect.

Carcinogenic risk analysis of OBDCRs by dermal contact

In non-sensitive areas, when a single contaminant in OBDCRs causes cancer through dermal contact, the calculation formula for the carcinogenic risk value of dermal contact is expressed by Eqs. 2 and 3 (China 2014).

$$\mathrm{CR_{dcs}} = \frac{\mathrm{SAE_a} \times \mathrm{SSAR_a} \times \mathrm{EF_a} \times \mathrm{ED_a} \times E_{\mathrm{v}} \times \mathrm{ABS_d}}{\mathrm{BW_a} \times \mathrm{AT_{ca}}} \times C_{\mathrm{OBDCR}} \times \frac{\mathrm{SF_o}}{\mathrm{ABS_{gi}}} \times 10^{-6} \quad (2)$$

$$\mathrm{SAE_a} = 239 \times H_{\mathrm{a}}^{0.417} \times \mathrm{BW_a}^{0.517} \times \mathrm{SER_a} \quad (3)$$

where $\mathrm{CR_{dcs}}$ (unitless) is the carcinogenic risk value of a single contaminant in OBDCRs during dermal contact, $\mathrm{SAE_a}$ (cm^2) is the exposure superficial area of adults' skin, $\mathrm{SSAR_a}$ (mg/cm^2) is the adherence rate of soil on the skin for adults, E_{v} (1/day) is the daily exposure frequency of dermal contact events, $\mathrm{ABS_d}$ (unitless) is the absorption efficiency of dermal contact, $\mathrm{ABS_{gi}}$ (unitless) is the absorption efficiency coefficient of the digestive tract, H_{a} (cm) is the average height of adults, and $\mathrm{SER_a}$ (unitless) is the skin exposure ratio of adults. Other parameters are the same as in Eq. 1.

Carcinogenic risk analysis of OBDCRs inhaled by breathing

In non-sensitive areas, when a single pollutant in OBDCRs is carcinogenic after inhalation, the formula for calculating the carcinogenic risk value is expressed by Eqs.4 and 5 (China 2014).

$$\mathrm{CR_{pis}} = \mathrm{PISER_{ca}} \times C_{\mathrm{OBDCR}} \times \frac{\mathrm{IUR} \times \mathrm{BW_a}}{\mathrm{DAIR_a}} \quad (4)$$

$$\mathrm{PISER_{ca}} = \frac{\mathrm{PM_{10}} \times \mathrm{DAIR_a} \times \mathrm{ED_a} \times \mathrm{PIAF} \times (\mathrm{fspo} \times \mathrm{EFO_a} + \mathrm{fspi} \times \mathrm{EFI_a})}{\mathrm{BW_a} \times \mathrm{AT_{ca}}} \times 10^{-6} \quad (5)$$

where $\mathrm{CR_{pis}}$ (unitless) is the carcinogenic risk value of a single contaminant in OBDCRs after inhalation, IUR (m^3/mg) is the carcinogenic coefficient per unit weight of inhalation, $\mathrm{DAIR_a}$ (m^3/day) is the daily air inhalation rate of adults, $\mathrm{PISER_{ca}}$ (kg (OBDCRs)/kg (height) day) is the content of inhalable OBDCRs particulates, $\mathrm{PM_{10}}$(mg/m^3) is the content of inhalable particulates in ambient air, PIAF (unitless) is the retention fraction of inhaled particulates in body, fspi (unitless) is the fraction of OBDCR particulates in indoor air, fspo (unitless) is the fraction of OBDCR-bome particulates in outdoor air, EFI_a (d/a) is the indoor exposure frequency of adults, and EFO_a (d/a) is the outdoor exposure frequency of adults. Other parameters are the same as in Eq. 1

Carcinogenic risk analysis of drinking groundwater

When OBDCRs are used to pave a well site, OBDCRs around the well site are leaching and soaking in rainwater. With the migration and diffusion of the shower solution, the contaminants in OBDCRs can dissolve and diffuse into the groundwater. The shower dissolution process is shown in Fig. 3. In non-sensitive areas, when people drink groundwater with contaminants, they are putting themselves at continued risk condition for cancer. The formula for calculating the carcinogenic risk value of drinking groundwater is expressed by Eq. 6 (China 2014).

$$CR_{cgw} = \frac{GWCR_a \times EF_a \times ED_a}{BW_a \times AT_{ca}} \times C_{gw} \times SF_o \qquad (6)$$

where CR_{cgw} (unitless) is the carcinogenic risk value of drinking groundwater containing contaminants in OBDCRs, $GWCR_a$ (L/day) is the daily groundwater consumption rate of adults, and C_{gw} (mg/L) is the concentration of contaminants in groundwater. Other parameters are the same as in Eq. 1.

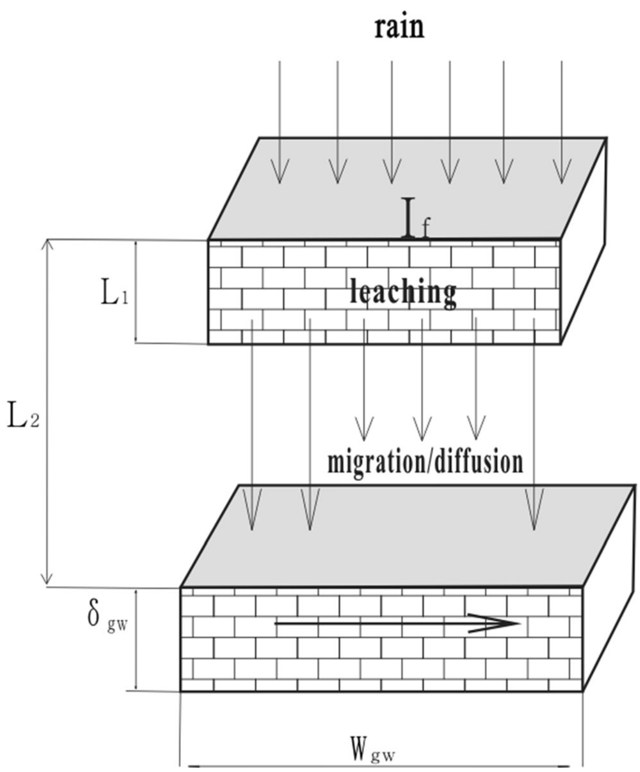


Fig. 3 Dissolving and diffusing of contaminants in OBDCRs into groundwater

Total carcinogenic risk of contaminants in OBDCRs

The total carcinogenic risks of contaminants in OBDCRs (CR_n) refer to the total carcinogenic risks of all the exposure pathways of a single pollutant. The calculation formula is expressed by Eq. 7 (China 2014).

$$CR_n = CR_{ois} + CR_{dcs} + CR_{pis} + CR_{cgw} \qquad (7)$$

Health risk assessment caused by NORM radioactivity

Absorbed dose rate

In this study, the absorbed dose rate is the total energy absorbed by a human body in the air 1 m above the ground, which comes from ^{226}Ra, ^{232}Th, and ^{40}K radioactive materials. Its calculation formula is expressed by Eq. 8 (UNSCEAR 1998; Joel et al. 2018).

$$Dc = 0.642C_{Ra} + 0.604C_{Th} + 0.0417C_K \qquad (8)$$

where Dc (Gy/h) is the absorbed dose rate at 1 m above OBDCRs, and C_{Ra}, C_{Th}, and C_K are NORM radionuclide concentrations in the OBDCR samples with the unit of Bq/kg.

Raeq

Generally, the level of radionuclides emitted from ^{226}Ra, ^{232}Th, and ^{40}K in OBDCRs is non-uniformly distributed. In this study, the radium equivalent radioactivity was used to compare the radioactivities of Ra (226), Th (232), and K (40) in the OBDCR samples. The unit of radium equivalent radioactivity (Raeq) is Bq/kg, and its formula is expressed by Eq. 9 (Joel et al. 2018).

$$Raeq = C_{Ra} + 1.43C_{Th} + 0.077C_K \qquad (9)$$

Hex

The external hazard index is the sum of the ratios of the specific radioactivities of natural radionuclides, which are Ra (226), Th (232), and K (40), to their limit values when they exist alone. External hazard index (Hex) (unitless) was calculated using Eq. 10 (Joel et al. 2018).

$$Hex = (C_{Ra}/370) + (C_{Th}/256) + (C_K/4810) \qquad (10)$$

Internal hazard index

The internal hazard index is the sum of the ratios of the specific radioactivities of Th (232) and K (40) to their limit values when they exist alone and the specific radioactivity of Ra

(226) to its limit value when its half exists alone. H_{in} (unitless) was calculated using Eq. 11 (Joel et al. 2018).

$$H_{in} = (C_{Ra}/185) + (C_{Th}/259) + (C_K/4810) \quad (11)$$

I_γ

The gamma index was used to evaluate the hazard of gamma rays emitted from natural radionuclides in the OBDCR samples. Gamma index (I_γ) (unitless) was calculated using Eq. 12 (Joel et al. 2018).

$$I_\gamma = (C_{Ra}/300) + (C_{Th}/200) + (C_K/3000) \quad (12)$$

I_α

The alpha index is another important parameter for hazard assessment, which is used to estimate the excessive alpha radiation caused by radon released from inhaled materials. Alpha index (I_α) (unitless) was calculated using Eq. 13 (Joel et al. 2018).

$$I_\alpha = \mathrm{C}_{Ra}/200 \quad (13)$$

Results and discussion

Chemical composition

In this study, the three OBDCR samples (YG-1, YG-2, and YG-3) were dark brown with a heavy odor and their petroleum hydrocarbon contents were 1.24–1.28%. The density was about 2.23 g/cm^3. The particle size was distributed in the range of 1–300 μm, and the maximum diameter did not exceed 0.2 mm. According to the SEM pattern, the shape of the OBDCRs particles was very irregular, their surfaces were porous and loose, and their microstructure showed a laxity shape (Fig. 4). The main mineral compositions were quartz (SiO_2), barite ($BaSO_4$), calcite ($CaCO_3$), aluminosilicate ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), and hematite ($Fe_2O_3$) (Table 1; Fig. 5). The loss on ignition was large, with an average value of 18.77%. The mineral composition and contents in OBDCRs determine the strategy of the utilization of these resources. According to the test results, their mineral composition and contents, the loss on ignition, and the particle size meet the requirements of the technical guidelines for the construction of highway road bases (China 2015). Therefore, OBDCRs have the potential to be used as the binder for the base or subbase of highways.

Heavy metal contents in the OBDCR samples

According to the national list of hazardous wastes (China 2016) and the identification standards for the general specifications of hazardous wastes (China 2007b), the hazardous characteristic of OBDCs is toxicity (*T*). The residues of OBDCs after treatment are still hazardous wastes. Therefore, Chongqing Ecological Environment Bureau instructed that OBDCRs should be managed as hazardous wastes. When analyzing the hazard characteristics of OBDCRs, toxicity was the focus of this study.

Based on the test results, there are more than 10 kinds of heavy metal elements in the OBDCR samples (Table 2). The content values of Cu, Zn, Cr, Pb, Ni, and As were very high, while for Ba and Mn, there are no relevant standard for comparison. Although these content values were lower than the standard screening values specified in the standard (China 2018a), the maximum measured content values of Cu, Zn, As, and Ni in this study were higher than 50% of the standard screening values for each corresponding heavy metal element. So the content values of four heavy metal elements (Cu, Zn, Ni, and As) were considered to be the main

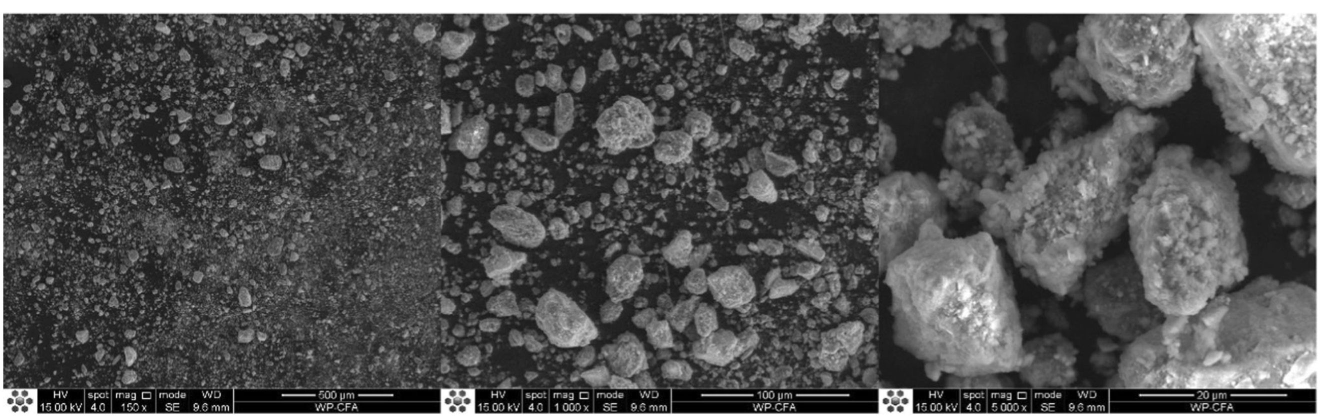


Fig. 4 SEM pattern of the OBDCR samples

Table 1 Chemical composition of the OBDCR samples (%, wt./wt.)

Sample	SiO_2	BaO	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	SrO	Loss
OBDCRs	42.18	9.70	6.36	3.02	6.94	1.37	1.31	1.74	7.67	0.32	0.24	18.77

parameters for evaluating the heavy metal carcinogenesis risks in the OBDCR samples.

Organic matter in the OBDCR samples

The organic matter contents in the OBDCR samples were analyzed by FT-IR and GC-MS, whose results are shown in Table 3. According to the GC-MS analysis results, the organic matter in the OBDCR samples mainly includes hydrocarbons, non-hydrocarbons, resins, and asphaltenes. Alkyl mercury, aniline, PAHs, volatile organic compounds are toxic substances.

Table 3 shows that there were many organic matters detected in the OBDCR samples such as benzopyrene (a), dibenzoanthracene (a, h), petroleum hydrocarbons, benzoanthracene (a), benzofluoranthene (b), benzofluoranthene (k), and indenopyrene (1,2,3-c, d). The content values of benzopyrene (a), dibenzoanthracene (a, h), and petroleum hydrocarbons exceeded the standard limit values specified in "soil environmental quality control standard for soil pollution risk of construction land" (China 2018b). The content value of benzoanthracene (a) was higher than 50% of the standard limit value. The total amount of carcinogenic PAHs was less than the standard limit value (0.1%) of the content identification toxic substances specified in the hazardous waste identification standard (China 2007a). But the six PAHs (benzoanthracene (a), benzopyrene (a), dibenzoanthracene (a, h), benzofluoranthene (b), benzofluoranthene (k), and indenopyrene (1,2,3-c, d)) had potential hazards to human health. Their content values were also considered to be the main parameters for evaluating the PAH carcinogenesis risks in the OBDCR samples.

Carcinogenic risk analysis

From the above section, we can see that the OBDCR samples contained many heavy metals and PAHs. According to the risk exposure model recommended by the Ministry of Ecology and Environment of China (China 2014), the OBDCRs can be directly used for roadbed materials (100%) only if the impact of heavy metals and PAHs in OBDCRs can be cleared.

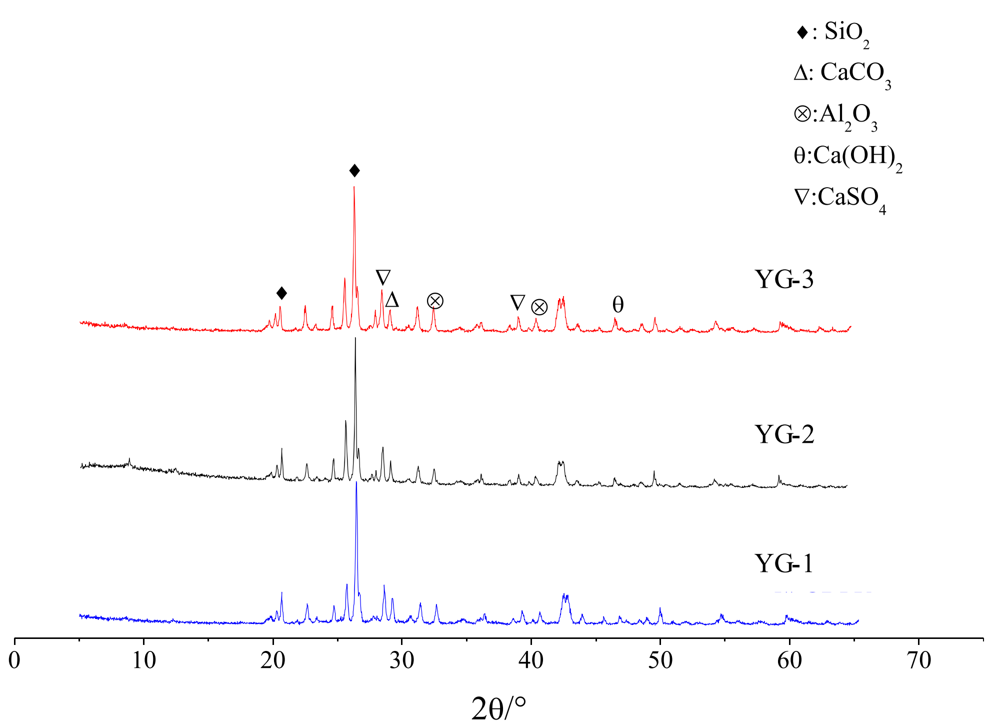


Fig. 5 XRD spectrum of the three OBDCR samples

Table 2 Heavy metal contents in the OBDCR samples

Heavy metals	Mean content values, mg/kg	Background content values, mg/kg	Agricultural land control standard (China 2018a)	Construction land control standard (China 2018b)
Cu	38.33	2.3	100	18000
Zn	161.67	120	250	NA
Cr	32.30	1.32	200	NA
Pb	36.93	8.9	120	800
Ba	3509.67	-	NA	NA
Ni	59.10	10.5	100	900
V	76.73	-	NA	752
Mn	223.00	657.0	NA	NA
Co	8.24	-	NA	70
As	13.80	0.08	30	60

NA indicates that there is no relevant standard value

Table 3 Organic matter content in the OBDCR samples

Organic matter	Mean content values, mg/kg	Agricultural land control standard (China 2018a)	Construction land control standard (China 2018b)
Naphthalene, mg/kg	0.74	NA	70
Acenaphthene, mg/kg	0.33	NA	NA
Acenaphthene, mg/kg	0.61	NA	NA
Fluorene, mg/kg	0.51	NA	NA
Phenanthrene, mg/kg	3.74	NA	NA
Anthracene, mg/kg	14.12	NA	NA
Fluoranthene, mg/kg	1.26	NA	NA
Pyrene, mg/kg	1.71	NA	NA
Benzophenanthrene (1,2), mg/kg	1.43	NA	1293
Benzoanthracene (a), mg/kg	7.78	NA	15
Benzofluoranthene (b), mg/kg	1.29	NA	15
Benzofluoranthene (k), mg/kg	6.14	NA	151
Benzopyrene (a), mg/kg	2.07	NA	1.5
Dibenzoanthracene (a, h), mg/kg	5.40	NA	1.5
Benzoperylene (g, h, I), mg/kg	8.09	NA	NA
Indenopyrene (1,2,3-c, d), mg/kg	0.65	NA	15
Petroleum hydrocarbon, mg/kg	12528.14	NA	4500

NA indicates that there is no relevant standard value

Hazard identification

According to Table 3, many heavy metals and PAHs in the OBDCR samples were detected such as Cu, Zn, Ni, As, benzoanthracene (a), benzopyrene (a), and dibenzoanthracene (a, h) whose content values were higher than 50% of the standard values. However, some slope factors were lacking for Cu, Zn, Ni, and other heavy metals and PAHs (Table 4). So, the carcinogenic risk was evaluated by considering only As, benzoanthracene (a), benzopyrene (a), dibenzoanthracene (a, h), benzofluoranthene (b), benzofluoranthene (k), and indenopyrene (1,2,3-c, d).

In this study, OBDCRs were assumed to be used as roadbed materials and laid on the inter-well-roads around the drilling platform. These experimental sites belong to industrial land and non-sensitive land, without any covering and anti-seepage treatments. The parameters used in this study were taken from the technical guidelines for the risk assessment of contaminated sites (China 2014). The concentrations of contaminants in groundwater (C_{gw}) were taken from the risk assessment report of shale gas development project. The parameter values of the seven pollutants (As, benzoanthracene (a), benzopyrene (a), dibenzoanthracene (a, h), benzofluoranthene (b), benzofluoranthene (k) and indenopyrene (1,2,3-c, d)) are shown in Table 5.

Evaluation results

Due to the lack of the reference doses of benzofluoranthene (b), benzofluoranthene (k) and indenopyrene (1,2,3-c, d) for drinking groundwater, the total carcinogenic risk values of benzofluoranthene (b), benzofluoranthene (k), and indenopyrene (1,2,3-c, d) were calculated based on the ingestion, inhalation, and dermal absorption pathways.

According to Fig. 6, the carcinogenic risk was calculated for As, benzoanthracene (a), benzopyrene (a), dibenzoanthracene (a, h), benzofluoranthene (b), benzofluoranthene (k), and indenopyrene (1,2,3-c, d). Among the carcinogenic risk computed for each pollutant, dibenzoanthracene (a, h), As, benzopyrene (a), and benzoanthracene (a) accounted for 55%, 18%, 16%, and 8%, respectively, while benzofluoranthene (b), benzofluoranthene (k), and indenopyrene (1,2,3-c, d) contributed only 1% each. So, the computed results showed that dibenzoanthracene (a, h), As, benzopyrene (a), and benzoanthracene (a) were the major contributors to the cancer risk.

In the carcinogenic risk of the PAHs, ingestion (CR_{ois}) and dermal (CR_{dcs}) pathways were the most prominent exposure pathways, accounting for 99% of the total risk value. In the carcinogenic risk of heavy metals, the ingestion pathway (CR_{ois}) had a decisive effect, accounting for 77% of the total risk value, followed by the dermal

Table 4 Parameters used in the carcinogenic risk assessment (China 2014)

	IUR, mg/m^3	SF_o, mg/(kg day)	ABS_{gi}, unitless		IUR, mg/m^3	SF_o, mg/(kg day)	ABS_{gi}, unitless
Cu	-	-	1	Acenaphthene	-	-	1
Zn	-	-	1	Anthracene	-	-	1
Cr^{6+}	84	0.5	0.025	Benzoanthracene (a)	0.11	0.73	1
Pb	-	-	-	Benzopyrene (a)	1.1	7.3	1
Ba	-	-	-	Benzofluoranthene (b)	0.11	0.73	1
Ni	0.26	-	0.04	Benzofluoranthene (k)	0.11	0.073	1
V*	8.3	-	0.026	Chrysene	0.011	0.0073	1
Mn	-	-	-	Dibenzoanthracene (a, h)	1.2	7.3	1
Co	9	-	1	Fluoranthere	-	-	1
As	4.3	1.5	1	Fluorine	-	-	1
				Indenopyrene (1,2,3-c, d)	0.11	0.73	1
				Naphthalene	0.034	-	1
				Pyrene	-	-	1

pathway (CR_{dcs}) and the inhalation pathway (CR_{pis}). For the cancer risk, the ingestion (CR_{ois}) and dermal (CR_{dcs}) pathways were the major pathways (Figs. 7 and 8).

Figure 8 shows that the total carcinogenic risk value (CR_n) of dibenzoanthracene (a, h) was the largest and that of benzofluoranthene (k) was the lowest. From the computed results, we can see that the total carcinogenic risk values (CR_n) of As, benzoanthracene (a), benzopyrene (a), and dibenzoanthracene (a, h) were all higher than 10^{-6} (China 2016). These values exceeded the control limit of the cumulative carcinogenic risk values specified in the technical guidelines for the environmental risk assessment of sites in Chongqing, showing that these values were at an unacceptable level. The total carcinogenic risk values (CR_n) of benzofluoranthene (b), benzofluoranthene (k), and indenopyrene (1,2,3-c, d) were all less than 10^{-6} (China 2016), showing that these values were at an acceptable level. And those carcinogenic contaminants with total carcinogenic risk values less than 10^{-6} were not considered to have significant adverse effects.

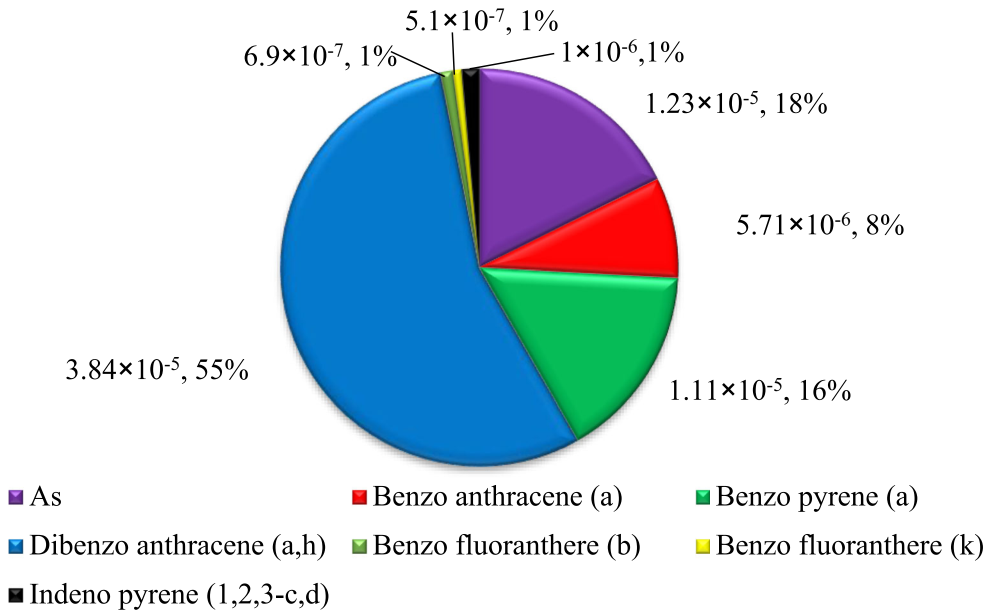
The cumulative value of the total carcinogenic risks in the OBDCR samples ($CR_{n,\ T}$) was 6.97×10^{-5}, which was at an unacceptable level. The result indicated that 69.7 persons in the 1,000,000 population may suffer from cancer due to the heavy metal and PAHs contaminations in OBDCRs. In conclusion, if OBDCRs were directly used to make roadbed materials (100%), there are great risks for the carcinogenic environment and human health. To reduce the total carcinogenic risk value to less than 10^{-6}, it is necessary to change the strategy of the utilization of OBDCRs such as producing cement (Wang et al. 2017b), sintered brick (Bernardo et al. 2007), and ceramics (Xiong et al. 2019). A legal standard and liability for utilization of OBDCRs assolid waste resources should be established, which needs to be enforced for OBDCRs treatment and utilization service companies.

Table 5 Parameter values for the carcinogenic risk assessment for OBDCRs used as roadbed materials

	Benzoanthracene (a)	**Benzopyrene (a)**	**Dibenzoanthracene (a, h)**	**Benzofluoranthene (b)**	**Benzofluoranthene (k)**	**Indenopyrene (1,2,3-c, d)**
Mean content value, mg/kg	10.53	2.07	7.17	1.29	9.21	1.95
C_{gw}, mg/L	2.56×10^{-5}	1.52×10^{-6}	1.61×10^{-6}	-	-	-
	Cu	**Zn**	**Ni**	**V***	**As**	
Mean content value, mg/kg	38.3	163	59.1	76.7	15	
C_{gw}, mg/L	-	-	-	-	1.26×10^{-6}	

The significance of the asterisk means vanadium

Fig. 6 Distribution of each parameter in the carcinogenic risk



Health risk assessment of NORM radioactivity

The radioactivity concentrations of Ra (226), Th (232), U (238), and K (40) in the OBDCR samples were measured and analyzed systematically. The results (Table 6) showed that the radioactivity concentration in the OBDCR samples ranged in 97.7–100 Bq/kg for Ra (226), 26.3–27.8 Bq/kg for Th (232), 22.6–33.5 Bq/kg for U (238), and 389–412 Bq/kg for K (40), respectively. The mean radioactivity concentration values of Th (232) and U (238) were found to be within the background values when compared with the reported ones (China 2019). But the mean radioactivity concentration value of Ra (226) was larger than the background value, and the radioactivity concentration of 40 K was the highest in the OBDCR samples. So, it was observed that the OBDCR samples had high radionuclide concentrations.

According to the health risk assessment of NORM radioactivity in the OBDCR samples (Table 7), the average absorbed dose rate was 96.54 nGy/h, which was higher than the international recommended value of 80 nGy/h (UNSCEAR 1998). However, the radium equivalent radioactivity (Raeq) ranged in 166.76–171.09 Bq/kg, which was less than the international recommended value of 370 Bq/kg (UNSCEAR 1998). The external hazard index (Hex), the internal hazard index, the gamma index (I_γ), and the alpha index (I_α) for those samples were less than 1. The I_γ value was less than 1, which was equivalent to the annual effective dose of less than or equal to 1 mSv. The I_α value was less than 1,

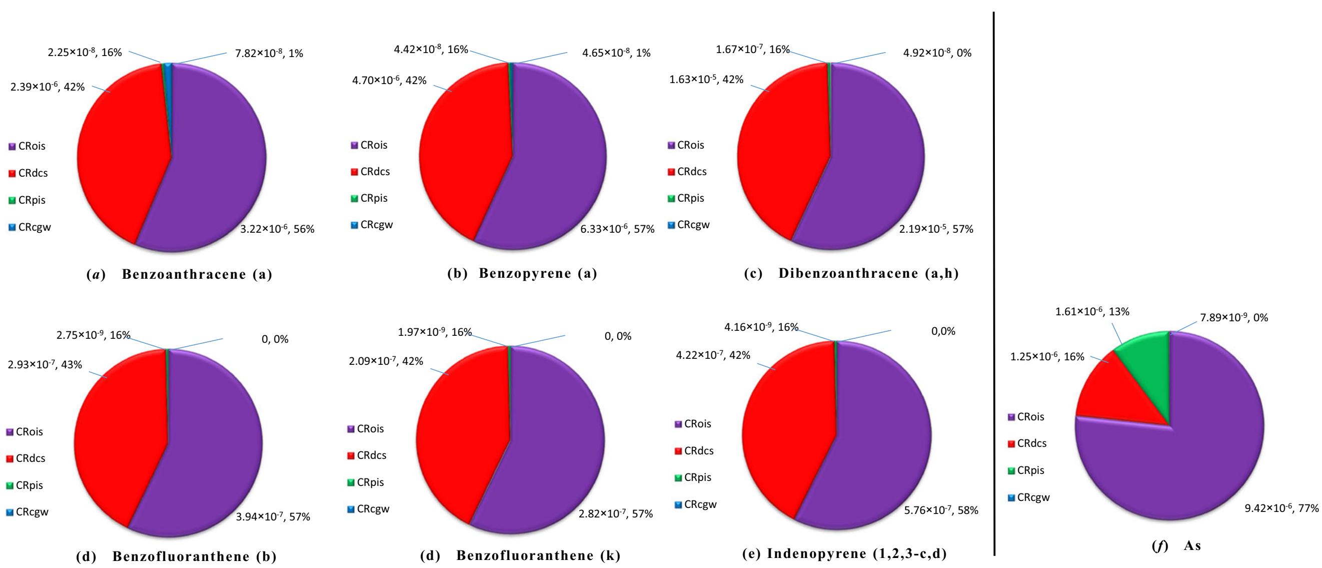


Fig. 7 Exposure pathway distribution of each pollutant in carcinogenic risk

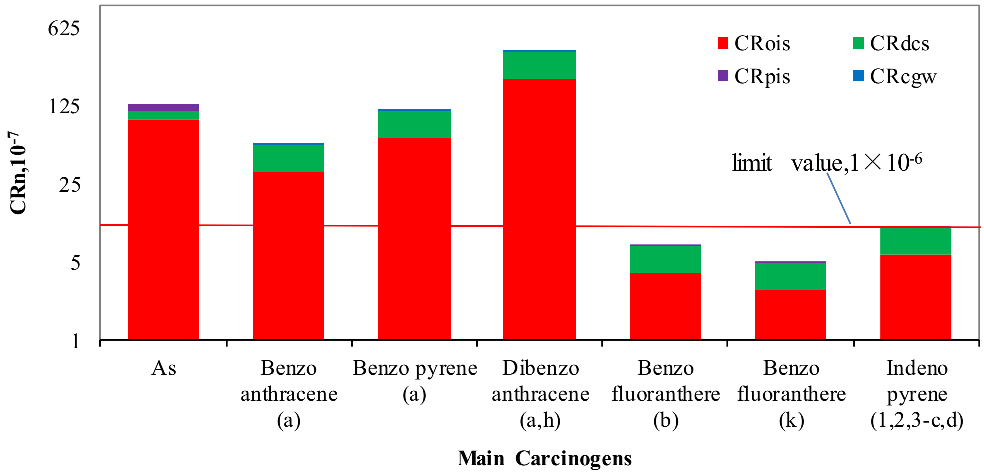


Fig. 8 Calculation results of carcinogens in the OBDCR samples

which was equivalent to that of the radon concentration in the air which is less than 200 Bq/m^3. Therefore, this result indicated that the health risk of NORM radioactivity in the OBDCR samples was low. The possible health risk may be caused by long-term exposure to radionuclides in OBDCRs. So it is suggested to reduce the health risk of NORM radioactivity in OBDCRs by changing the working hours and service years of the recycled OBDCRs.

Conclusion and suggestion

OBDCRs have the potential to be used for building materials. However, the OBDCRs contain many kinds of carcinogenic contaminants such as heavy metal elements, PAHs, and NORMs, which are great risks for the environment and human health. The measurements showed that the concentration values of benzopyrene (a), diphenylanthracene (a, h), and petroleum hydrocarbons in the OBDCR samples exceeded the standard limit. The concentration values of Cu, Zn, As, and Ni were higher than 50% of the standard limit. When OBDCRs were directly used to make roadbed materials, the total carcinogenic risk values (CR_n) of As, benzoanthracene (a), benzopyrene (a), and dibenzoanthracene (a, h) were all higher than 10^{-6}, which were in the unacceptable level. The external hazard index, the internal hazard index, the gamma index, and the alpha index were less than 1. The average total carcinogenic risk values of Th (232) and U (238) in the OBDCR samples were in the range of the background values. However, the average absorbed dose rate was higher than the international recommended value of 80 nGy/h. Therefore, if OBDCRs were directly used to pave roads, the heavy metals, PAHs, and NORMs will be great potential risks to human health. So, in the process of utilization of OBDCRs, it is necessary to consider the strategy of the utilization method, the working time, and the service life of the recycled OBDCRs

Table 6 Radioactive intensity distribution in the OBDCR samples

	C_{Ra226}, Bq/kg	C_{Th232}, Bq/kg	C_{K40}, Bq/kg	C_{U238}, Bq/kg
YG-1	99.2	26.3	389	33.5
YG-2	97.7	26.4	412	29.1
YG-3	100	27.8	407	22.6
Background values	23.0-29.0	39.0-52.0	-	27.0–53.0

Table 7 Health risk assessment of NORM radioactivity in the OBDCR samples

	Dc, nGy/h	Raeq, Bq/kg	Hex, unitless	Hin, unitless	I_γ, unitless	I_α, unitless
YG-1	95.79	166.76	0.45	0.72	0.50	0.52
YG-2	95.85	167.18	0.45	0.72	0.49	0.53
YG-3	97.96	171.09	0.46	0.73	0.50	0.54
Recommended values	80	370	1	1	1	1

and establish a legal standard and liability for the utilization of OBDCRs as solid waste resources.

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Chao-qiang Wang: assisting with research, experiments, and data analysis.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Declarations

Ethical approval Any experimental research on animals should follow the internationally recognized guidelines. However, in this study, we did not conduct any human or animal experiments, so we do not need the moral consent of the relevant departments.

Consent to participate Nobody participated in the human or animal experiment.

Consent for publication All authors agreed to publish the article.

Competing interests The authors declare no competing interests.

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