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Migration Behaviors of As, Se and Pb in Ultra-Low-Emission Coal-Fired Units and Effect of Co-Firing Sewage Sludge in CFB Boilers

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Abstract: The migration behaviors of As, Se and Pb in ultra-low-emission coal-fired units were investigated and the effect of co-firing of sewage sludge and coal was explored in circulating fluidized-bed (CFB) boiler units. Samples of feed fuel including coal and sewage sludge, fly ash, bottom slag and desulfurization slurry were collected from five CFB units with a capacity between 150 MW and 350 MW and two pulverized coal boiler (PC) units with a capacity of 350 MW and 600 MW. The majority of As, Se and Pb in coal is released during coal combustion and enriched in fly ash. As, Se and Pb in fly ash and bottom slag are associated with inorganic matter, of which As, Se and Pb associated with silicates and aluminosilicates account for more than 60%. In the wet flue gas desulfurization (WFGD) unit, more than half of the As, Se and Pb migrates to the solid fraction and the concentrations of As, Se and Pb in fine solid particles are much higher than those in coarse solid particles and the liquid fraction. The proportions of exchangeable As, Se and Pb or associated with organic matter in gypsum are higher than those of fly ash and bottom slag. According to the two studied CFB units with blending ratios of sewage sludge below 10%, co-firing with sewage sludge has little effect on the migration and transformation characteristics of As, Se and Pb. Under a long-term acidic leaching environment, Pb in combustion by-products is in the range of low risk, while As and Se are in the range of medium risk.

Keywords: As; Se; Pb; coal-fired power units; co-firing sewage sludge; migration; environmental risk

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1. Introduction

Arsenic (As), selenium (Se) and lead (Pb) are extremely toxic trace elements for human health due to their mobility, bioaccumulation and persistent toxicity [1,2]. Coal combustion for electricity and heat generation is the main source of anthropogenic trace element emissions [3]. Many countries have established strict emission standards. For example, the Environmental Protection Agency of the United States formulated the first national Clean Air Act standards to reduce toxic trace element emissions from coal-fired power units [4]. Although China has not stipulated the relevant emission limits for As, Se and Pb, the Ministry of Environmental Protection proposed to address the prevention and control of harmful trace elements as key issues of environmental protection [5,6]. At the same time, a large amount of sewage sludge is generated from wastewater treatment plants in modern industrial countries [7,8]. Co-firing coal with sewage sludge, biomass and other non-fossil energy in coal-fired power units is currently considered one of the most suitable processes for the resource utilization of waste, which could reduce CO_2 net emission from coal combustion [9]. It is disappointing that only a few studies have focused on the effect of co-firing with sewage sludge on the migration behaviors of As, Se and Pb in coal-fired power units. Therefore, it is of great significance to study the migration behaviors and environmental risks of As, Se and Pb in combustion by-products and the effect of co-firing sewage sludge.

It is difficult to directly measure the concentrations of As, Se and Pb in coal and its combustion by-products due to the complex structure and extremely low content of trace elements. Thus far, the indirect measurement method has been widely used for the evaluation of trace element in coal and combustion by-products, which transfers solid into solution. Therefore, the digestion procedure is of importance for guaranteeing the accuracy of test data. Three kinds of digestion methods developed are drying ash digestion, wet digestion and microwave-assisted digestion. The conventional ash drying digestion method treats coal using a mild combustion process and the obtained ash is subsequently dissolved with nitric acid, which leads to the possible volatilization loss of some elements during the ash fusion process [10]. In the conventional wet digestion method, solid samples are pretreated with oxidation and acidification by various acid solutions in an unsealed container [11]. The main disadvantage of the conventional wet digestion method is the tedious experimental procedures and volatilization loss of elements during the digestion process in an open vessel at high temperatures. Therefore, microwave-assisted acid digestion has been widely used for the pretreatment of solid samples in recent years [12–14]. Microwave-assisted digestion takes advantage of the characteristics of heating the solution both inside and outside, which makes the heating process more rapid and uniform. In addition, microwave-assisted digestion is performed in a sealed high-pressure digestion tank with an overheating phenomenon. The sample can be heated to a higher temperature than the boiling point under atmospheric pressure, which can greatly improve the digestion efficiency and dissolve the samples that cannot be digested by general wet digestion [15]. The detection methods of As, Se and Pb in digestion solution mainly include atomic absorption spectrometry (ASS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and hydride generation atomic fluorescence spectrometry (HG-AFS). Compared with other methods, HG-AFS has strong element selectivity and less interference lines, which makes the measurement accuracy up to one part per billion [16].

Large amounts of combustion by-products are generated from traditional coal-fired power units. The fly ash of fine particles and desulfurized gypsum is usually used as building materials. In contrast, the fly ash of coarse particles and bottom slag is subjected directly to landfill treatment [17]. As, Se and Pb may be released secondarily during the process of resource utilization and leak to the groundwater and soil in the storage process of coal combustion by-products [18–20]. The migration and toxicity characteristics of trace elements are heavily dependent on their speciation in coal and its combustion by-products [18,21,22]. Despite the fact that different methods, such as the float–sink test, statistical analysis and direct test analysis, have been suggested to determine the speciation of trace elements, they are hardly in good agreement, mainly due to the complicated chemical structure of coal together with extremely low concentrations of As, Se and Pb. Compared with other methods, the sequential chemical extraction (SCE) procedure, originally developed by Tessier et al. [23], was improved and is regarded as a reliable method to determine different kinds of trace elements in coal and its combustion by-products [24–26]. This method is dependent on a specific extractant to extract the fraction of elements in samples sequentially according to their differences in solubility. To the best of our knowledge, only a few reports have verified the occurrence regularity of As, Se and Pb speciation in ultra-low-emission power units.

At present, pulverized coal boilers (PC) and circulating fluidized-bed boilers (CFB) are the two main types of boilers used in coal-fired power units, of which the CFB has been popularly utilized for co-firing with low-calorific-value coal or sewage sludge due to its inherent advantages, such as good fuel adaptability and blending, relatively low-temperature combustion and lower pollutant emissions [27,28]. Previous studies [29–31] focused on the effects of the combustion temperature and boiler type on the mineralogical composition of fly ash and bottom slag, but there are few comparative analyses of the effects on the distribution and enrichment of As, Se and Pb. In order to achieve stricter pollutant emission standards, ultra-low-emission air pollution control devices (APCDs) have been vigorously promoted and widely applied in coal-fired power units in China. A typical ultra-low-emission power unit is equipped with a selective catalytic reduction (SCR)/ selective non-catalytic reduction (SNCR) denitrification system, a particulate control device, such as an electrostatic precipitator (ESP) and fabric filter (FF), a wet flue gas desulfurization (WFGD) unit and a wet electrostatic precipitator (WESP). The synergistic removal of As, Se and Pb by ultra-low-emission APCDs is one of the most cost-effective technologies, and different types of APCDs have various removal effects on As, Se and Pb [32,33]. Fu et al. [21] and Cordoba et al. [34] showed that the concentrations of As, Se and Pb in desulfurized gypsum were generally lower than those in fly ash, but were more unstable; in other words, As, Se and Pb in desulfurized gypsum were more harmful to the environment than fly ash. At the same time, desulfurized gypsum slurry can be divided into the solid phase and liquid phase, which need to be studied separately and extensively. It should be mentioned that the majority of previous investigations were based on PC boiler units, whilst only a few considered circulating fluidized-bed (CFB) boiler units [35,36].

In this study, samples of feed fuel, fly ash, bottom slag and desulfurization slurry were collected from five CFB units with a capacity between 150 MW and 350 MW, two of which were co-firing with sewage sludge. Two PC units with the capacity of 350 MW to 600 MW were also selected to investigate the effect of boiler type on As, Se and Pb emissions from ultra-low-emission coal-fired power units. The main contents are the following: (1) the migration and transformation behaviors of As, Se and Pb in feed fuel and combustion by-products of coal-fired power units; (2) comparison of the As, Se and Pb emission behaviors between PC units and CFB units; (3) effect of co-firing with sewage sludge on the As, Se and Pb emissions from coal-fired power plants; (4) environmental risk assessment of As, Se and Pb in combustion by-products. The aim of this study was to further understand the migration and transformation characteristics of As, Se and Pb in the ultra-low-emission coal-fired power units and the effect of co-firing with sewage sludge on them, which could provide guidance for the control of As, Se and Pb emissions.

2. Materials and Methods

2.1. Sample Collection

Samples of feed fuel, bottom slag, fly ash and desulfurization slurry were collected from five CFB units with a capacity between 150 MW and 350 MW and two PC units with a capacity of 350 MW to 600 MW, which are listed in Table 1. The sampling processes were performed under stable and continuous operating conditions of the coal-fired power units. Each sample was collected at the corresponding sampling position in triplicate and then quickly sealed in Teflon bottles. After being ground and sieved under 65 μm, the feed fuel samples were dried at 105 °C to a constant weight and then packaged for later experiments. Proximate analysis results of feed fuel samples were obtained with an automatic industrial analyzer, and these are presented in Table 2. Slurry samples collected from WFGD units were filtered to obtain the liquid fraction and the corresponding solid fraction. Three parts were observed from the slurry samples, namely the liquid fraction in the top section, the dark brown-colored solid fraction in the middle section (fine particle fraction) and the light-colored solid fraction in the bottom section (coarse particle fraction). The solid fractions obtained from slurry were dried at 45 °C to a constant weight.

Table 1. Unit capacity, air pollution control devices and samples of coal-fired power units.

Units	Unit Capacity	Air Pollution Control Devices	Samples
CFB1	150 MW	SCR [1] + FF [2] + WFGD [3]	Feed fuel + Fly ash + Bottom slag + Gypsum
CFB2	200 MW	SCR + FF + WFGD	Feed fuel + Fly ash + Bottom slag + Gypsum
CFB3	300 MW	SNCR [4]/SCR + FF + WFGD	Feed fuel + Fly ash + Bottom slag + Slurry
CFB4	300 MW	SCR + FF + WFGD	Feed fuel + Fly ash + Bottom slag + Slurry
CFB5	350 MW	SCR + FF + WFGD + WESP [5]	Feed fuel + Fly ash + Bottom slag + Slurry
PC1	350 MW	SCR + ESP [6] + WFGD + WESP	Feed fuel + Fly ash + Bottom slag + Slurry
PC2	600 MW	SCR + ESP + WFGD + WESP	Feed fuel + Fly ash + Bottom slag + Slurry

[1] SCR—selective catalytic reduction; [2] FF—fabric filter; [3] WFGD—wet flue gas desulfurization; [4] SNCR—selective non-catalytic reduction; [5] WESP—wet electrostatic precipitator; [6] ESP—electrostatic precipitator.

Table 2. Proximate analysis of feed fuel samples from coal-fired power units.

Power Units	Fuel Type	Proximate Analysis/wt%			
		M_{ad} [1]	A_{ad} [2]	V_{ad} [3]	FC_{ad} [4]
CFB1	Coal	1.86	13.29	33.52	51.33
	Sewage sludge	3.65	61.51	18.16	16.68
CFB2	Coal	1.24	61.20	18.62	18.94
CFB3	Coal	2.36	33.96	24.94	38.74
CFB4	Coal	2.38	39.76	24.74	33.12
CFB5	Coal	1.04	54.19	14.44	30.33
	Sewage sludge	3.53	59.21	25.79	11.47
PC1	Coal	2.67	15.05	29.95	52.33
PC2	Coal	3.98	16.42	25.57	54.03

[1] M—moisture content, ad—air drying basis; [2] A—ash content; [3] V—volatile content; [4] FC—fixed carbon content.

2.2. Determination of As, Se and Pb Concentrations in Solid Samples

Solid samples collected from coal-fired power units, including coal, sewage sludge, fly ash, bottom slag and gypsum, were digested by a microwave digestion instrument, and the concentrations of As, Se and Pb were measured by an AFS. The procedures of the microwave digestion method were as follows.

Stage 1: The sample was weighed at 0.1 ± 0.001 g and mixed with the digestion solution of 2.0 mL hydrochloric acid (HCl), 6.0 mL nitric acid (HNO_3) and 2.0 mL hydrofluoric acid (HF) in a Teflon digestion tank, which was then sealed and placed in the microwave digestion instrument. The Teflon tank was heated from room temperature to 220 °C by the temperature programming method and maintained for a period, and then cooled below 80 °C by automatic air intake. After this, the digestion tank was taken out and placed in the fume hood.

Stage 2: The inner wall of the digestion tank was washed with ultra-pure water, and then the solution in the tank was transferred to the Teflon beaker. Then, the Teflon beaker was placed on the electric heating plate at 140 °C to evaporate the acid until the solution in the Teflon beaker was approximately 1 mL.

Stage 3: The Teflon beaker was rinsed with ultra-pure water three times and the solution was transferred to a 100 mL volumetric flask. A certain amount of HCl was added to the volumetric flask and then diluted with ultra-pure water to a constant volume. The amounts of HCl for As, Se and Pb were 3.0 mL, 10.0 mL and 1.0 mL, respectively. In addition, when the measured element was As, 5.0 g thiourea needed to be added to the volumetric flask and heated in a constant-temperature water bath at 50 °C for 30 min.

Current-carrying reagent and reducing reagent need to be prepared in advance for HG-AFS, which are formulated exclusively for As, Se and Pb, respectively. For As, the current-carrying agent is 3% HCl solution and the reducing agent is 0.5% potassium hydroxide (KOH) and 1% potassium borohydride (BH_4K) mixed solution; for Se, the current-carrying agent is 10% HCl solution and the reducing agent is 0.2% KOH and 1% BH_4K mixed solution; for Pb, the current-carrying agent is 1% HCl solution and the reducing agent is 1% KOH, 1% BH_4K and 1% potassium ferricyanide ($K_3[Fe(CN)_6]$) mixed solution.

Further details of the procedures can be obtained from our previous work [37].

2.3. Determination of As, Se and Pb Speciation in Solid Samples

In the modified sequential chemical extraction (SCE) procedure, magnesium chloride ($MgCl_2$) solution was used first to remove exchangeable As, Se and Pb, followed by HCl to remove the As, Se and Pb fraction associated with carbonates, sulfates and oxides, and then hydrofluoric acid (HF) to remove the fraction with silicates and aluminosilicates; finally, we used HNO_3 to remove the fraction with sulfides, whilst the unextracted As, Se and Pb in the residue was assumed to be present in the organic matrix. The above reagents were of analytical grade, and deionized water was used in all procedures. Experimental containers were made of glass or Teflon to avoid the loss of adhered As, Se and Pb, which were previously soaked in 20% (v/v) HNO_3 and rinsed with deionized water. The leached solution was filtered and analyzed for As, Se and Pb by a AFS analyzer, whilst the residue in the final stage was digested as described in Section 2.2 and then measured using the AFS analyzer. All tests were performed three times and the average values were regarded as the fraction of As, Se and Pb extracted at each stage. As shown in Figure 1, a detailed explanation of the SCE procedure is as follows.

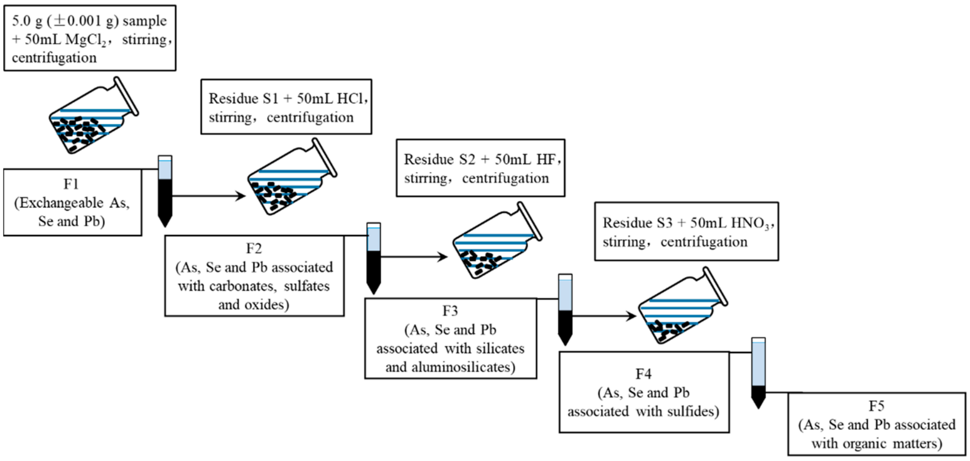


Figure 1. Schematic diagram of sequential chemical extraction method.

Stage 1: First, 5.0 g ± 0.001 g sample was extracted with 50.0 mL ± 0.15 mL $MgCl_2$ to extract the exchangeable As, Se and Pb (F1).

Stage 2: The residue from Stage 1 was extracted with HCl solution (5 M) to dissolve the As, Se and Pb associated with carbonates, sulfates and oxides (F2).

Stage 3: The residue from Stage 2 was extracted with HF (40%) to dissolve the As, Se and Pb associated with silicates and aluminosilicates (F3).

Stage 4: The residue from Stage 3 was extracted with HNO_3 (4 M) to extract the As, Se and Pb associated with sulfides (F4). The residue obtained from this stage was free of F1, F2, F3 and F4, which indicates that the As, Se and Pb in it is associated with organic matter (F5).

In order to guarantee the analytical precision of As, Se and Pb as trace elements existing in coal, a mass balance was used to examine the reliability of the SCE procedure. The recovery ratios of As, Se or Pb in each sample were between 88% and 109%, 75% and 102% and 92% and 113%, respectively, which were in the range of the 70% to 130% limitation suggested by the U.S. Environmental Protection Agency [38]. The recovery ratio ranges were caused by the loss of SCE process, the interference of external element pollution and measurement error.

2.4. Environmental Risk Assessment Methods of As, Se and Pb in Combustion By-Products

In order to investigate the environmental risk of As, Se and Pb in combustion by-products, the leaching behaviors of As, Se and Pb in combustion by-products were evaluated in detail by the toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP) and multiple extraction procedure (MEP) methods. TCLP simulates the leaching risk of As, Se and Pb in combustion by-products in a moderately acidic environment [39]; SPLP predicts the migration behaviors of As, Se and Pb in combustion by-products under acid rain conditions [40]; MEP can evaluate the leaching behavior of As, Se and Pb in combustion by-products under long-term repeated leaching conditions [41]. Detailed explanations of the above methods are as follows.

The TCLP test was performed with 20:1 liquid-to-solid ratio; 5.0 g ± 0.001 g of sample was added into a 100 mL Teflon bottle and 100 mL of acetic acid solution with the pH of 2.9 was added. The bottle was subsequently horizontally vibrated for 18 ± 2 h at room temperature.

The SPLP test was performed with 20:1 liquid-to-solid ratio; 5.0 g ± 0.001 g of sample was added into a 100 mL Teflon bottle and 100 mL of H_2SO_4 and HNO_3 mixture solution with the pH of 3.2 and mass ratio of 2:1 was added. The bottle was subsequently horizontally vibrated for 18 ± 2 h at room temperature.

The MEP test was first performed as with the TCLP method, and then the obtained sample was extracted by the SPLP method at least 9 times. If the As, Se and Pb concentrations in the extraction solution still increased compared with the eighth time, the extraction process was repeated until the concentrations of As, Se and Pb in the extraction solution did not increase.

3. Results and Discussion

3.1. Migration of As, Se and Pb in Coal-Fired Power Units

3.1.1. Migration of As, Se and Pb in Furnace

The three CFB units and two PC units in this study only used coal as feed fuel. The mean concentrations and standard deviations of As, Se and Pb in feed coal, fly ash and bottom slag samples from the five coal-fired power units are presented in Figure 2. The concentration of As in the coal ranged from 2.18 μg/g to 3.50 μg/g, which is below the average As concentration in Chinese coal (5.00 μg/g) [42]. The concentration of Se was in the range of 3.93–5.19 μg/g, which is slightly higher than the average Se concentration in Chinese coal (2.00 μg/g). Different from As and Se, the concentration of Pb in coal from CFB units and PC units showed different regularity, i.e., the concentration of Pb in coal from CFB units ranged from 16.38 to 21.54 μg/g, which is higher than the average Pb concentration in Chinese coal (13.00 μg/g), while that in PC units was in the range of 8.01–8.22 μg/g, which is below the average Pb concentration in Chinese coal. According to the proximate analysis of feed fuel between CFB units and PC units in Table 2, the speciation distribution characteristics of As, Se and Pb in feed coal are different.

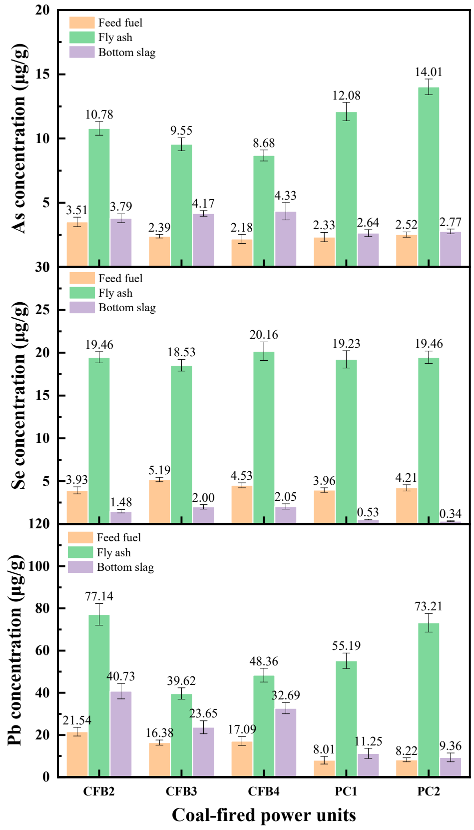


Figure 2. Distribution characteristics of As, Se and Pb in feed coal, fly ash and bottom slag of coal-fired power units.

During coal combustion in a furnace and with flue gas flowing through air pollution control devices, As, Se and Pb in feed coal would migrate to different solid residues, such as fly ash and bottom slag. As shown in Figure 2, As, Se and Pb in coal present different volatilization characteristics. The concentrations of As, Se and Pb in fly ash are significantly higher than those in feed coal, with ranges of 8.68–14.01 μg/g, 18.53–20.16 μg/g and 39.62–77.14 μg/g, respectively. The concentrations of As and Pb in bottom slag are slightly higher than those in feed coal, with ranges of 2.64–4.33 μg/g and 9.36–40.73 μg/g, respectively. Meanwhile, the concentration of Se in bottom slag is extremely low, ranging from 0.34 μg/g to 2.05 μg/g, implying that As, Se and Pb show differences in volatilization during the coal combustion process and then tend to condense on the fly ash particles at low temperatures. The release process of trace element compounds in coal during combustion can be summarized as the following three steps [43]: (1) trace element compounds transfer from the interior of particles to the surfaces of particles; (2) trace element compounds gasify on the surfaces of particles; (3) trace element compounds transfer to the outside main airflow through the particle pores. The concentrations of As, Se and Pb in fly ash from the PC units were generally higher than those from the CFB units, while those in the bottom slag of PC units were lower than those of CFB units, indicating that temperature is the main factor determining the volatilization behaviors of As, Se and Pb in coal.

As, Se and Pb compounds connected by weak bonds in coal are oxidized and decomposed in a CFB at a combustion temperature between 800 °C and 950 °C, while As, Se and Pb compounds with high thermal stability can be decomposed and released in the PC boiler with a combustion temperature above 1300 °C. Liu et al. [44] found that the volatilization ratio of As in coal was between 17% and 60% when the combustion temperature was 900 °C, and rose to 90% when the combustion temperature was up to 1500 °C. The calculation result of thermodynamic equilibrium by Contreras et al. [45] indicated that Se in coal is mainly volatilized to the gas phase SeO_2 at 850 °C. Zhang et al. [46] found that Pb in coal usually exists in galena and is mainly released in the form of $PbCl_2$ or PbS. As a result, the release of Pb can be enhanced with the decomposition of galena within the temperature range between 800 °C and 1200 °C. In addition, fly ash contains a large percentage of metal oxides, such as Fe_2O_3 and CaO [20,21,26], providing enough absorbability to react with the As and Se existing in the flue gas to form arsenate and selenate compounds (Equations (1)–(4)) [47].

$$\mathrm{CaO(s) + As_2O_3(g) + O_2(g) \rightarrow Ca_3(AsO_4)_2(s)} \tag{1}$$

$$\mathrm{Fe_2O_3(s) + As_2O_3(g) + O_2(g) \rightarrow FeAsO_4(s)} \tag{2}$$

$$\mathrm{SeO_2(g) + CaO(s) \rightarrow CaSeO_3(s)} \tag{3}$$

$$\mathrm{SeO_2(g) + Fe_2O_3(s) \rightarrow Fe_2(SeO_4)_3(s)} \tag{4}$$

The tested coal-fired power units were equipped with SCR denitrification technology. The flue gas is usually cooled down to the range between 280 °C and 420 °C when it flows through SCR. Kong et al. [48] proposed that As_2O_3 would be adsorbed and oxidized on the catalyst surface, forming a dense layer on the catalyst surface by the eventual product As_2O_5. NH_3-SCR tests conducted by Liu et al. [49] confirmed that Se could be oxidized to Se^{4+} (SeO_2 and $V_xSe_yO_z$) by the catalyst; meanwhile, part of Se^{4+} was reduced to Se by NH_3. ESP and FF are the two main types of particulate control devices installed in coal-fired power units to capture particulates from flue gas, which can influence the migration behaviors of the gaseous trace elements and remove particulate trace elements in the flue gas. Previous studies [26,29] confirmed that the synergistic removal efficiency of As, Se and Pb in flue gas by particulate control devices of ultra-low-emission units is over 90%.

In order to better evaluate the enrichment characteristics of As, Se and Pb in fly ash and bottom slag, the relative enrichment factor (REF), proposed by Meij et al. [50] and frequently utilized in previous studies [29,32,33], was calculated according to Equations (5) and (6):

$$REF_{i,\ fly\ ash} = \frac{C_{i,fly\ ash} \times C_{ash\ in\ coal}}{C_{i,coal}} \tag{5}$$

$$REF_{i,\ bottom\ slag} = \frac{C_{i,bottom\ slag} \times C_{ash\ in\ coal}}{C_{i,coal}} \tag{6}$$

where $\mathrm{REF_{i,\ fly\ ash}}$ is the relative enrichment factor of As, Se or Pb in fly ash; $\mathrm{REF_{i,\ bottom\ slag}}$ is the relative enrichment factor of As, Se or Pb in bottom slag; $\mathrm{C_{i,\ fly\ ash}}$ is the concentrations of As, Se or Pb in fly ash; $\mathrm{C_{i,\ bottom\ slag}}$ is the concentrations of As, Se or Pb in bottom slag; $\mathrm{C_{i,\ coal}}$ is the concentrations of As, Se or Pb in coal, and $\mathrm{C_{ash\ in\ coal}}$ is the ash content in coal (given in Table 2).

Due to the different properties of feed fuel, diverse combustion conditions in the furnace and various APCDs, the enrichment characteristics of As, Se and Pb in fly ash and bottom slag vary significantly. As shown in Figure 3, the REFs of As, Se and Pb in fly ash are in the ranges of 0.78–1.88, 0.73–3.03 and 0.82–2.19, respectively. Meanwhile, the REFs of As, Se and Pb in bottom slag range from 0.17 to 0.79, 0.01 to 0.23 and 0.19 to 1.16, respectively, which are significantly lower than those of fly ash. Meanwhile, the REFs of As, Se and Pb in bottom slag of CFB units are higher than those in PC units. Compared with PC units, the lower combustion temperatures of CFB units result in lower release ratios of As, Se and Pb from coal, which leads to larger proportions of residual As, Se and Pb in the bottom slag. It can be found in Table 2 that the feed coal used in CFB units usually has high ash content, which has significant proportions of mineral impurities to provide sufficient absorption capability for As, Se and Pb [51]. In addition, the migration behaviors of As, Se and Pb in coal-fired power units are not only affected by different types of boilers and APCDs, but also affected by the properties of the fly ashes. Marczak-Grzesik et al. [52] and Bartoňová et al. [53] found that the fly ash of CFB units has high unburned carbon content, an irregular shape, a rough surface and more honeycomb pores, which leads to greater amounts of As, Se and Pb enriched in fly ash from CFB units compared to PC units.

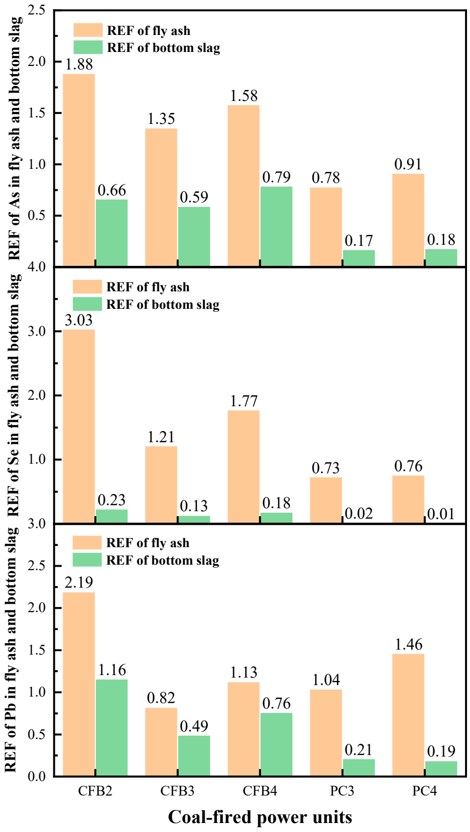


Figure 3. REFs of As, Se and Pb in fly ash and bottom slag of coal-fired power units.

3.1.2. Migration of As, Se and Pb in WFGD Units

Slurry samples were collected from WFGD units, with approximately 8.70–13.84% in the solid phase, which were centrifuged to obtain the liquid fraction and the solid fraction, including the fine particle fraction and coarse particle fraction. The mean concentrations of As, Se and Pb in the three fractions obtained from WFGD slurry are summarized in Figure 4, which shows that the concentrations of As, Se and Pb in the gypsum were generally lower than those in fly ash because most of the As, Se and Pb in flue gas was captured by the fly ash through ESP or FF. An obvious result that can be observed from Figure 4 is that the concentrations of As, Se and Pb in fine particles were in the ranges of 3.86–10.47 μg/g, 1.02–7.01 μg/g and 0.78–7.66 μg/g, while those in coarse particles were in the range of 0.78–3.45 μg/g, 0.10–0.54 μg/g and 0.08–0.35 μg/g, respectively, which are obviously lower than those in fine particles. The concentrations of As, Se and Pb in the liquid fraction were extremely low, being lower than 0.29 μg/g. The main reason for this finding is that As, Se and Pb associated with sulfate are easily adsorbed on the surfaces of fine particles with a large specific surface area. In addition, the fine particles also contain a great deal of fine fly ash not captured by the particulate control devices, which is enriched with As, Se and Pb, thereby causing higher concentrations of As, Se and Pb in the fine particles [21]. As shown in Figure 3, the fly ash of PC units has lower enrichment capacity for As, Se and Pb than that of CFB units; as a result, more gaseous As, Se and Pb was not captured by the particulate control devices and entered into the WFGD unit.

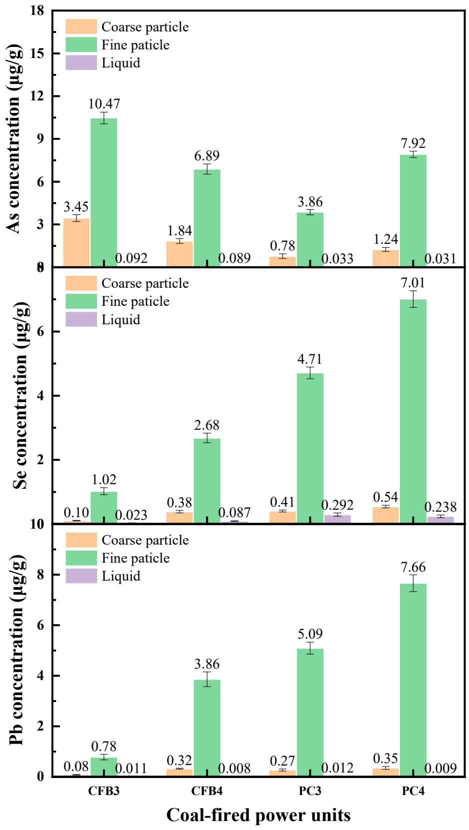


Figure 4. Concentrations of As, Se and Pb in coarse particles, fine particles and liquid fraction of WFGD slurry.

The mass distribution of fine particles, coarse particles and liquid in slurry was 6.28–10.91%, 0.87–3.09% and 86.16–90.98%, respectively. Combined with the mass distribution and the As, Se and Pb concentrations of the tress parts from the WFGD slurry, the mass distribution characteristics of As, Se and Pb are listed in Figure 5, which shows that more than 70% of As, 50% of Se and 90% of Pb migrated to the solid phase of the WFGD unit. Although the As, Se and Pb concentrations were extremely low in the liquid fraction, as shown in Figure 4, the mass proportion of the liquid fraction accounted for 86.16–90.98% of the total slurry, so there was still a considerable proportion of As, Se and Pb that migrated to the liquid fraction. Accompanied by a drop in flue gas temperature, Pb in the flue gas entering the WFGD unit is mainly in granular form, which is enriched in fine fly ash particles [26,32]. The fine particles are mainly generated by the fine fly ash that escapes from the particulate control devices. Compared with Se and Pb, As accounts for a higher proportion in coarse particles due to the high As concentration in limestone added to the WFGD unit. Meanwhile, part of the gypsum is mixed with calcium arsenate and calcium selenate formed by the gaseous arsenic oxide or selenium oxide [26].

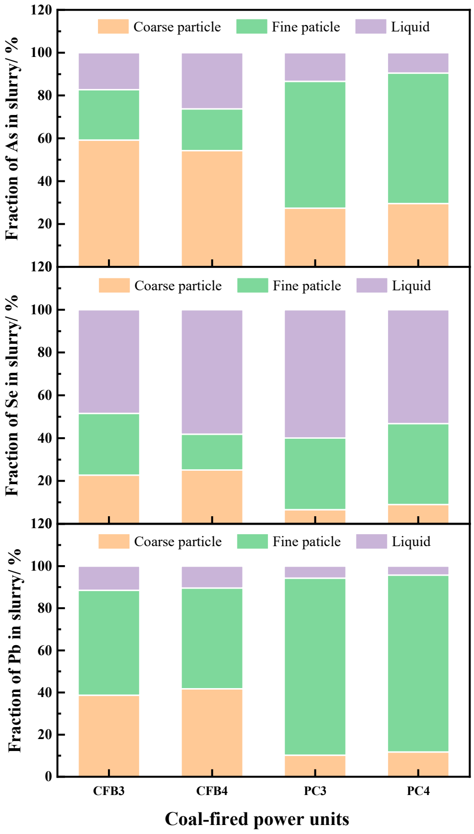
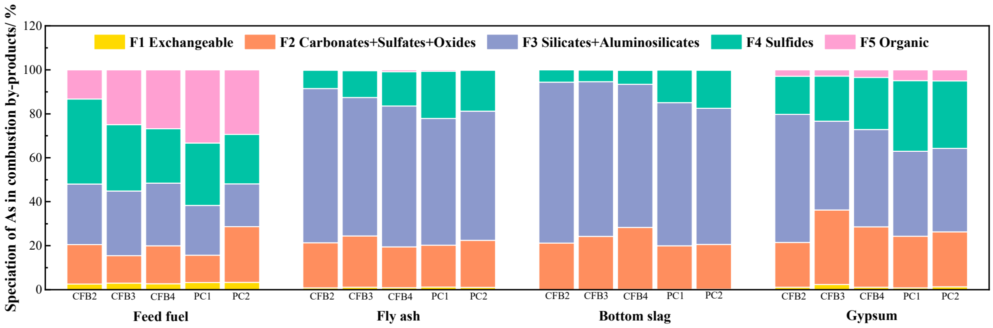


Figure 5. Partitioning of As, Se and Pb in coarse particles, fine particles and liquid fraction of WFGD slurry.

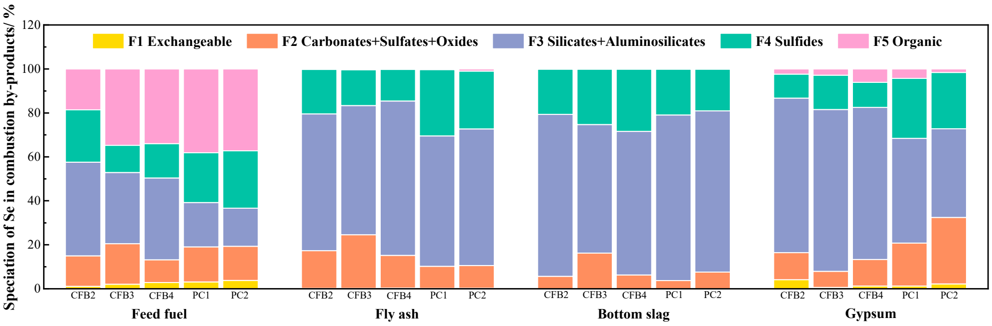
3.2. Speciation Transformation of As, Se and Pb in Coal-Fired Power Units

A modified sequential chemical extraction (SCE) method was employed to characterize the speciation of As, Se and Pb in feed fuel and combustion by-products. The content of each As, Se or Pb fraction from the SCE procedure was first converted to As, Se or Pb concentration distributions by each extraction stage. The concentration distribution was linked to the volume distribution of the leaching solution from each stage of extraction to transfer into the relative mass distribution of each As, Se or Pb fraction. Then, the relative content of each fraction of As, Se and Pb in the samples was obtained, as shown in Figure 6. The recovery ratios of As, Se and Pb in feed fuel and combustion by-products were 88–109%, 75–102% and 92–113%, respectively, which indicates the high reliability of the SCE results. The detailed analysis of the speciation of As, Se and Pb in feed coal and combustion by-products is as follows.

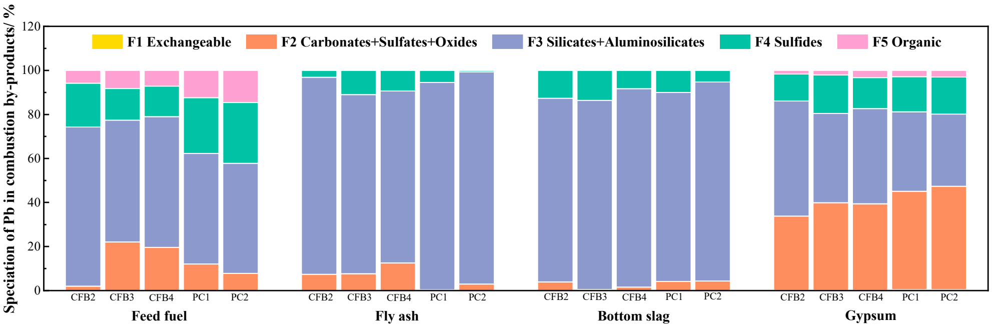
Each of these samples showed that F1 (exchangeable As) is generally not a major fraction of As, even though it was readily extracted from the samples. Most of the As in feed coal exists in inorganic forms, including As associated with carbonates, sulfates and oxides (F2), As associated with silicates and aluminosilicates (F3) and As associated with sulfides (F4). The proportions of F2, F3 and F4 were 12.37–25.29%, 18.27–33.67% and 22.48–38.69%, respectively. The proportion of As associated with organic matter (F5) was 13.25–33.30%, which is related to the volatile content of feed coal. Almost all the As in fly ash and bottom slag is inorganic, of which more than 60% of the As is associated with silicates and aluminosilicates (F3). Compared with fly ash and bottom slag, As in gypsum has higher proportions of F2 (As associated with carbonates, sulfates and oxides), F4 (As associated with sulfides) and F5 (As associated with organic matter), which may be caused by the speciation of As in limestone added to the WFGD.



(**a**) As



(**b**) Se



(**c**) Pb

Figure 6. Speciation distribution of As, Se and Pb in feed coal and combustion by-products of coal-fired power units.

The proportion of Se associated with organic matter (F5) in coal is higher than that of As, while Se associated with sulfides (F4) is less. Similar to As, most of the Se in fly ash and bottom slag is associated with silicates and aluminosilicates (F3). During the combustion process, Se in coal can be fused into the Fe-Si-Al lattice and adsorbed on the surface of fly ash by chemical reaction at 800 °C [54]. It is noteworthy that the proportion of Se associated with carbonates, sulfates and oxides (F2) in fly ash is higher than that of bottom slag, which indicates that gaseous Se is likely to condense on the fly ash surface as SeO_2 when the temperature of flue gas drops to 200 °C. The speciation distribution behavior of Se in gypsum is similar to that in fly ash, besides slightly higher proportions of F1 (exchangeable Se) and F5 (Se associated with organic matter). The gaseous Se that escapes from the particulate control devices can react with water to form H_2SeO_3, which then reacts with Ca^{2+} in the desulfurization slurry to form $CaSeO_3$ [55]. In the acidic environment of WFGD slurry, $CaSeO_3$ can dissolve in the supernatant and can be easily extracted as exchangeable Se (F1).

Pb in feed coal is mainly associated with silicates and aluminosilicates (F3), with the proportions ranging between 50% and 70%, and it is difficult to be released in the combustion process; thus, a considerable amount of Pb associated with silicates and aluminosilicates (F3) remains in the fly ash and bottom slag. In addition, there is approximately 20% Pb associated with carbonates, sulfates and oxides (F2) and sulfides (F4), which is likely to volatilize in the form of PbO in the gas phase when the temperature is above 1000 °C [56]. Then, PbO would react with chlorine in the flue gas to form $PbCl_2$, which can react with Al_2O_3 or SiO_2 in fly ash to be held in place by the silicon aluminate lattice at high temperatures [57].

Compared with feed coal, the proportion of Pb associated with silicates and aluminosilicates (F3) in fly ash or bottom slag increases to 80–90%, while the exchangeable Pb (F1) and Pb associated with organic matter (F5) are negligible. The proportions of Pb associated with carbonates, sulfates and oxides (F2) and sulfides (F4) in gypsum are 20–40% and 8–25%, respectively, which are significantly higher than those in fly ash or bottom slag. Most of the Pb in the WFGD unit comes from limestone or fly ash that has escaped from the particulate control devices. Only a small amount of gaseous Pb enters the WFGD unit and reacts with desulfurization slurry to form compounds such as $PbSO_4$, which are then adsorbed to the surface of gypsum.

3.3. Effect of Co-Firing of Coal with Sewage Sludge

Sewage sludge and coal have different compositions and structural characteristics. Sewage sludge is mainly composed of low-level organic matter, the structure of which is relatively simple. Furthermore, it has been treated by secondary biological oxidation and damaged by decomposition in different degrees, making it easy to decompose at high temperature. Coal is mainly composed of polycyclic aromatic hydrocarbons with a dense structure and high carbon content, and it needs a longer time and higher temperature to be decomposed. The blending ratios of sewage sludge in the CFB1 unit and CFB5 unit were 5% and 10%, respectively, which had little effect on the concentrations of As, Se and Pb in feed fuel. As shown in Figure 7, the concentrations of As, Se and Pb in the feed fuel of the two units were 2.87 μg/g, 4.98 μg/g, 8.47 μg/g and 6.73 μg/g, 7.98 μg/g, 17.09 μg/g, respectively, which are still low amounts of As, Se and Pb in coal according to the content classification of harmful elements in coal. Furthermore, the enrichment and distribution characteristics of As, Se and Pb in combustion by-products are mainly affected by the properties of the coal and the combustion temperatures of the two units. In contrast to other coal-fired power units, the concentration and REF of Pb in bottom slag are higher than those of fly ash in CFB1, as shown in Figure 8. The small capacity and low-load operation condition of CFB1 cause a low combustion temperature in the boiler, which leads to less Pb released from coal. Although some researchers [58,59] have shown that a higher chlorine concentration in sewage sludge can accelerate the release of As, Se and Pb, the sewage sludge blending ratio of less than 10% had no significant impact during the actual operation of the power units in this study. It can be found in Figure 9 that the speciation distribution of As, Se and Pb in feed fuel and combustion by-products of CFB1 and CFB5 were in the ranges of coal-fired power units shown in Figure 6.

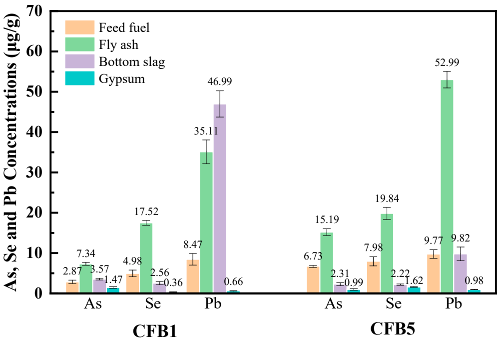


Figure 7. Distribution characteristics of As, Se and Pb in feed fuel, fly ash, bottom slag and gypsum of CFB1 and CFB5.

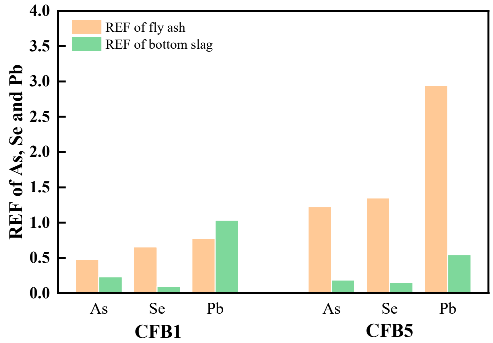
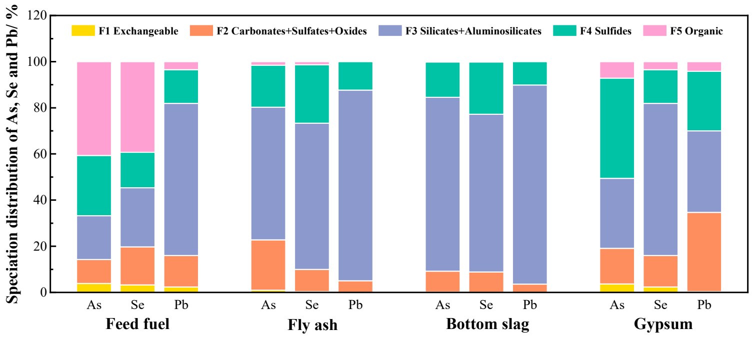
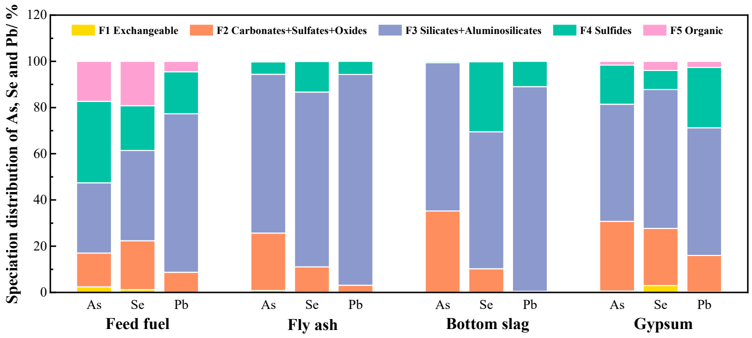


Figure 8. REFs of As, Se and Pb in fly ash and bottom slag of CFB1 and CFB5.



(**a**) CFB1

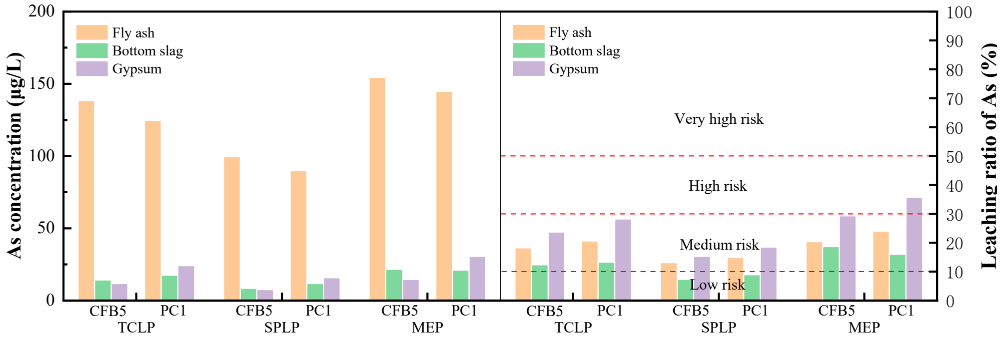


(**b**) CFB5

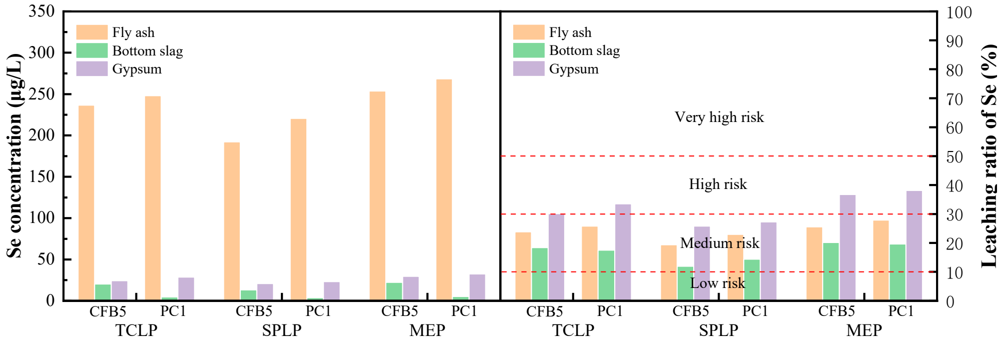
Figure 9. Speciation distribution of As, Se and Pb in feed fuel and combustion by-products of CFB1 and CFB5.

3.4. Environmental Risk Assessment of As, Se and Pb in Combustion By-Products

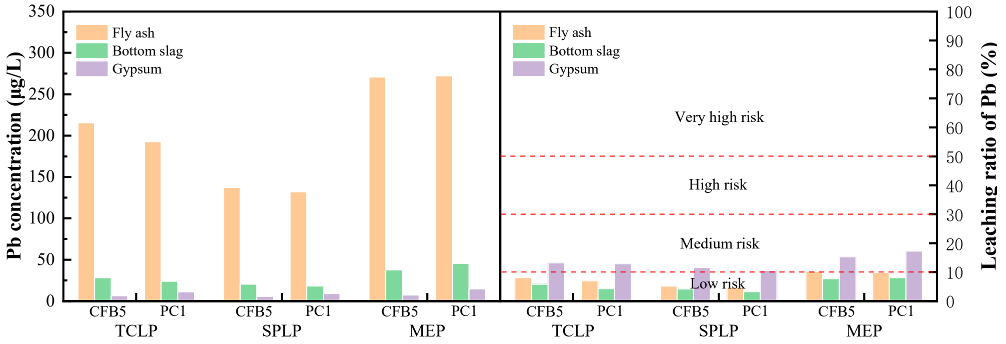
CFB5 and PC1, with the same capacity of 350 MW but significant differences in feed fuel properties, were taken as examples, which were treated with TCLP, SPLP and MEP to conduct the leaching experiments. The results are shown in Figure 10. In general, the concentrations of As, Se and Pb in the leaching solution of MEP were higher than those of TCLP and SPLP, while the concentrations of As, Se and Pb in the leaching solution were the lowest in SPLP. It can be inferred that the As, Se and Pb in combustion by-products do not easily leach into the environment under the condition of short-term acid rain erosion but would gradually enter the environment during a long-term repeated leaching process. The concentrations of As, Se and Pb in the leaching solution of fly ash are much higher than those of bottom slag and gypsum. The main reason is that the concentrations of As, Se and Pb in fly ash are higher than those of bottom slag and gypsum. In addition, a large amount of gaseous As, Se and Pb is condensed and adsorbed on the surface of fly ash with a decrease in flue gas temperature. Some of the gaseous As, Se and Pb reacted with Ca/Fe oxides on the surface of fly ash to form corresponding compounds, which were adsorbed on the surface of fly ash ultimately. Furthermore, Su et al. [60] found that the concentrations of K, Na, Ca and other alkali metal oxides in fly ash are higher than those of bottom slag and gypsum, which have a stronger neutralization effect on the acid leaching solution and provide a better pH environment for the leaching of As, Se and Pb in fly ash.



(**a**) As



(**b**) Se



(**c**) Pb

Figure 10. Leaching characteristics of As, Se and Pb in combustion by-products of CFB5 and PC1.

According to the leaching ratio, the environmental risks of As, Se and Pb in combustion by-products can be divided into five grades: less than 1% for no risk, 1–10% for low risk, 11–30% for medium risk, 31–50% for high risk and more than 50% for very high risk [18,61–63]. Pb of fly ash or bottom slag is in the range of low risk, while As and Se are at medium risk. Although the concentrations of As, Se and Pb in the leaching solution of fly ash are much higher than those of bottom slag and gypsum, the leaching ratios of As, Se and Pb in gypsum are the highest among the three types of combustion by-products. In the MEP method, As and Se in gypsum carry a high risk and Pb is at medium risk, which indicates that gypsum has a certain degree of harm to the environment under a long-term acidic leaching environment. Considering the large number of combustion by-products produced by power units and the complex landfill conditions or resource utilization processes, appropriate treatment measures need to be taken to minimize the harm to the environment.

4. Conclusions

The migration behaviors of As, Se and Pb in ultra-low-emission coal-fired units were investigated and the effect of co-firing with coal and sewage sludge was explored in circulating fluidized-bed (CFB) boiler units. Samples of feed fuel including coal and sewage sludge, fly ash, bottom slag and desulfurization slurry were collected from five CFB units with a capacity between 150 MW and 350 MW and two pulverized coal boiler (PC) units with a capacity of 350 MW and 600 MW. The main conclusions were obtained as below.

(1) The concentrations of As, Se and Pb in feed coal are 2.33–6.73 μg/g, 3.93–7.98 μg/g and 8.01–21.54 μg/g, respectively. Almost all Se is released to the gas phase after combustion and the residue concentration in the bottom slag is less than 2.56 μg/g. However, the concentrations of As and Pb are relatively higher in the bottom slag because of their less volatile nature, with residue concentrations of 1.96–4.33 μg/g and 9.36–46.99 μg/g. Generally, As, Se and Pb are mainly enriched in fly ash, with concentrations of 7.34–17.63 μg/g, 17.52–24.35 μg/g and 35.11–86.93 μg/g, respectively. Therefore, coal-fired power units should try to reduce the temperature of the flue gas in the particulate control devices to promote the condensation of gaseous As, Se and Pb, which could cause most of the As, Se, and Pb to be enriched in the fly ash for centralized treatment and reduce the emission of As, Se, and Pb. WFGD mainly collects As, Se and Pb in the fly ash particles that escape from the particulate control device, resulting in a small amount of As and Se in the gas phase. More than 70% of As, 50% of Se and 90% of Pb migrate to the solid phase of WFGD and the concentrations of As, Se and Pb in fine solid particles are much higher than those in coarse solid particles and the liquid fraction.

(2) The proportion of As or Se associated with organic matter (F5) in feed fuel ranges from 20% to 40%, while that of Pb is less than 10%. As, Se and Pb in both fly ash and bottom slag exist in the inorganic bound state, of which As, Se or Pb associated with silicates and aluminosilicates (F3) account for more than 60%. The proportions of As, Se and Pb existing in the exchangeable state (F1) or associated with organic matter (F5) in desulfurized gypsum are higher than those of fly ash and bottom slag.

(3) Compared with traditional coal-fired power units, when the sewage sludge blending ratio in co-firing sewage sludge CFB units is less than 10%, it has little effect on the migration and transformation behaviors of As, Se and Pb in fly ash, bottom slag and desulphurized gypsum.

(4) Under a long-term acidic leaching environment, Pb in combustion by-products is in the range of low risk, while As and Se are in the range of medium risk. The leaching ratios of As, Se and Pb in gypsum are the highest among the three types of combustion by-products.

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