J Radioanal Nucl Chem (2013) 295:1405–1411
DOI 10.1007/s10967-012-2165-4

Application of surface complexation modeling on the leaching of radionuclides from fly ashes

Liping Qian · Minghai Ma · Donghua Cheng

Received: 14 June 2012 / Published online: 13 September 2012
© Akadémiai Kiadó, Budapest, Hungary 2012

Abstract Surface complexation modeling based on diffuse double layer model (DDLM) has been employed to simulate the leaching behaviors of radionuclides (i.e., $^{60}Co^{2+}$, $^{63}Ni^{2+}$, $^{64}Cu^{2+}$ and $UO_2{}^{2+}$) on fly ashes from hospital wastes. The fly ashes were characterized by X-ray diffraction (XRD), potentiometric acid–base titration, and scanning electron microscopy (SEM). The effect of pH, the ratio of solid-to-liquid (RSL), and particle size on the leaching of radionuclides was also conducted under the batch techniques. According to XRD patterns analysis, the main components of fly ashes was determined to be quartz and clay minerals such as kaolinite, illite and smectite. The site density and pH_{PNZC} (pH at point of net zero charge) of fly ashes calculated from potentiometric titration data was found to be 4.53×10^{-4} mol/g and 7.4, respectively. One can see that the small amount of metal oxides attached on the surface of fly ashes by SEM images, corrosion surface of fly ashes was observed after leaching experiments. Results of the batch leaching experiments indicated that the leaching amount of radionuclides in fly ashes significantly depended on pH, the ratio of solid-to-liquid, and particle size. It is found that the leaching amount of radionuclides decreased in the order of $^{64}Cu^{2+} \gg {}^{63}Ni^{2+} > {}^{60}Co^{2+} > UO_2{}^{2+}$ under the different pH, the RSL or particle size conditions. In this paper, DDLM has successfully been applied to describe the leaching behaviors of radionuclides from fly ashes. This research provides critical information for application of surface complexation modeling on the simulation of radionuclides leaching from fly ashes, which would clarify the leaching mechanism of radionuclides from fly ashes.

Keywords Surface complexation modeling · Radionuclides · Leaching · Fly ashes

Introduction

Medical waste from hospitals and other healthcare institutions has become an imperative environmental and public safety problem, which has become one of the most urgent environmental problems in China after the outbreak of severe acute respiratory syndrome (SARS) in 2003 [1]. There are 14000 tons of medical wastes produced annually, of which only a small proportion is incinerated [2]. Incineration has become the main treatment method for medical waste disposals, which can be very effective in minimizing the most hazardous and infectious health-care waste. incineration processes, however, emit large amounts of particulate matter (PM) (e.g., bottom and fly ashes) and air pollution-control residues with high content of heavy metals [3], inorganic salts and other organic compounds (e.g., dioxins), as well as radionuclides [4].

Although the technological and economical benefits were the main reasons for the use of fly ashes such as adsorbents [5, 6], the prevention of environmental contamination by means of proper waste disposal becomes a priority. Fly ashes are hazardous to health when one inhaled or ingested due to occurrence of radionuclides in fly ashes [7], which can come back to human beings through the several channels such as bioaccumulation [8]. Enrichment of the radionuclides in fly ashes is observed during the combustion process. Most radionuclides are controlled and enforced to sequestrate under the limit of

L. Qian (✉) · M. Ma · D. Cheng
The School of Life Science and Environmental Science, Huangshan University, Huangshan 245041, People's Republic of China
e-mail: lpq@hsu.edu.cn

permission leaching by the sorption of clay minerals and quartz from fly ashes.

The chemical behaviors of radionuclides in fly ashes and other adsorbent have been studied in recent years extensively [9–13]. Zielinski et al. [14] studied the distribution and relative abundance of radionuclides in fly ash and bottom ash systematically and found uranium was largely dispersed within glassy components of fly ashes particles. Karangelos et al. [15] detailed the natural radioactivity of radionuclides (i.e., ^{238}U, ^{226}Ra, ^{232}Th and ^{210}Pb) of ashes from Greek lignite-fired power plants and concluded that the radioactivity of some natural nuclides was gradually enhanced. Rahman et al. [16] used different mathematical models (e.g., first-order reaction model, diffusion model and collective model) to simulate the leaching characteristics of radionuclides from incineration ashes. Surface complexation modeling (SCM) has also been employed to fit the interaction between radionuclides and adsorbents, such as U(VI) sorption on bentonite [17] and on kaolinite [18], Eu(III) sorption on MX-80 bentonite [19], Sr(II) sorption on hydrous zirconium oxide [20]. However, to our knowledge, few studies on simulation of leaching behaviors of radionuclides from fly ashes by using SCM technique have been observed.

In this study, the fly ashes were characterized by X-ray diffraction (XRD), potentiometric acid–base titration, and scanning electron microscopy (SEM). The leaching experiments of radionuclides from fly ashes as a function of pH, the ratio of solid-to-liquid (RSL) and particle size were investigated by batch technique. The purpose of this study was: (1) to characterize the microscopic and macroscopic properties of fly ashes, (2) to study the effect of pH, RSL and particle size on radionuclides leaching from fly ashes, and (3) to simulate the leaching behaviors of radionuclides from fly ashes by using SCM technique.

Experimental

Elemental component of fly ashes

Fly ashes used in this study were sampled from Huangshan People's Hospital waste incinerators, where located in the southern China (Fig. 1). The particle size of fly ashes were wet-sieved to obtain <2.0, 2–100 and 100–200 fractions, which corresponded to the clay fraction, sludge fraction, and sand fraction. It is found that approximately 90 % of sand fraction was observed in terms of gravitational separation methods [21], therefore the final products were ground to a particle size of less than 150–200 μm because this enhanced homogeneity and minimized occlusion occurring in large insoluble particles and speeded up equilibrium in leaching experiments.

Characterization of fly ashes

The elemental components of fly ashes were measured by X-ray fluorescence (XRF-2000, South Korean) analyzer. The fly ashes were characterized by XRD, potentiometric titration, and SEM. The XRD measurements were mounted by Cu Ka radiation generated in the Phillips XRG 300 X-ray diffractometer at step scan increment of 0.2° and a dwell time of 2 s. The potentiometric acid–base titration measurements were performed with a Mettler automatic titrator (DL5X, Switzerland) under N_2 conditions to eliminate the influence of atmospheric CO_2. Subsamples of the materials investigated of approximately 0.1 g in 40 mL 0.01 mol/L $NaClO_4$ were placed in a container maintained at 25 °C and equilibrated overnight with the electrolyte solution. The SEM measurements were recorded by using a field emission scanning electron microscope (FEI-JSM 6320F, Japan).

The batch leaching experiments

The leaching of $^{60}Co^{2+}$, $^{63}Ni^{2+}$, $^{64}Cu^{2+}$ and UO_2^{2+} from fly ashes as a functional of pH, RSL and particle size was investigated by batch technique. The radionuclide leachability was conducted by the acetic acid standard leaching test. A weighted amount of fly ashes were immersed in 500 mL leachate (acetic acid) and stirred vigorously for 8 h to obtain different pH, RSL and particle size at 20 °C under continuous stirring conditions. Afterwards, the suspensions were left undisturbed for more than 16 h to allow complete settling of the fly ashes. After 24 h of equilibrium, the final pH was recorded, and the suspensions were filtered through 0.2 μm membrane filters. The concentration of $^{60}Co^{2+}$, $^{63}Ni^{2+}$, $^{64}Cu^{2+}$ and UO_2^{2+} from aqueous solution was carried out with liquid scintillation counting (Packard 3100 TR/AB, PerkinElmer).

Application of surface complexation modeling

The geochemical speciation code PHREEQC version was used to simulate desorption reactions of $^{60}Co^{2+}$, $^{63}Ni^{2+}$, $^{64}Cu^{2+}$ and UO_2^{2+} from fly ashes. Parameters to the standard PHREEQC databases are presented in Table 3. Diffuse double layer model (DDLM) and database with surface complexation reactions has been employed in this study [22].

Results and discussion

Element analysis in fly ashes

The elemental components of fly ashes were tabulated in Table 1. The contents of metal oxides are very high (22.3 and 20.6 % as CaO and SiO_2 respectively). Most of the

Fig. 1 The fly ashes from incinerator of Huangshan People's Hospital (Huangshan, Anhui, Southeastern China)

radionuclides in the fly ashes are in the trace amount range of 0.001–0.01 %, including $^{64}Cu^{2+}$ (24.5 mg/kg), $^{63}Ni^{2+}$ (0.943 mg/kg), $^{60}Co^{2+}$ (0.376 mg/kg), and UO_2^{2+} (0.082 mg/kg). It is obvious to find that the concentration of copper in fly ashes is significantly higher than other radionuclides such as nickel, cobalt and uranium. Because hospital wastes in China usually contain high amount of plastic matter, which copper and nickel are usually used as additive in these plastics such as medical adhesive plaster, as well as in alloys for needle, syringe production and rubber from hospitals. For example, PVC used in medial apparatus generally contains copper, and this type of plastics also contains high levels of chlorine (Cl), which is consistent with the above element analysis (Cl, 8.6 %) very well. The other radionuclides (e.g., $^{63}Ni^{2+}$, $^{60}Co^{2+}$ and UO_2^{2+}) were also generally used in medicines, photographic materials and medial tools in the medical field.

Characterization of fly ashes

The fly ashes were characterized by XRD, potentiometric titration and SEM techniques (Fig. 2). As shown in Fig. 2a, the main components of fly ashes at <2 μm fraction exhibited the clay minerals, such as kaolinite, illite, and montmorillonite. It is worthwhile to point out that the iron oxide (e.g., hematite) was observed in terms of analysis of XRD patterns at <2 μm fraction. For fly ashes at 200–300 μm fractions, however, the only quartzes diffraction was found due to occurrence of the large number of quartzes at sand fraction.

The potentiometric acid–base titration was performed at 0.01 mol/L $NaClO_4$ in order to determine the surface properties of fly ashes. The site density (TOT_{SOH}) and pH_{PZC} (pH at point of zero charge) of fly ashes can be calculated by Eqs. (1) [23] and (2) [24] respectively:

$$TOT_{SOH} = 0.5 \times \left([H^+]_{sample+water} - [H^+]_{water}\right) \quad (1)$$

$$pH_{PZC} = 0.5 \times (pK_1 + pK_2) \quad (2)$$

where $[H^+]_{sample+water}$ and $[H^+]_{water}$ refers to the concentration of consumed H^+ with and without samples by acid titration from pH 11.0–3.0 respectively. The pK_1 and pK_2 are the surface acidity constants obtained from acid–base titration. As shown in Table 1, the total concentration of surface active sites was calculated to be 4.53×10^{-4} mol/g, the pH_{PZC} of fly ashes was calculated to be 7.4.

The morphology of fly ashes was characterized by SEM. As shown in Fig. 2c, d, the flake-like clay minerals coated metal oxides (black dots) in the fly ashes were observed before leaching experiments (Fig. 2c), which is consistent with of

Table 1 The elemental components of fly ashes from hospital waste incinerators

Components	CaO	SiO_2	SO_3	Cl	Al_2O_3	Fe_2O_3	ZnO	K_2O	Na_2O	MgO	TiO_2
Content (%)	22.3	20.6	17.9	8.6	7.2	7.9	3.86	1.55	3.2	2.4	2.4

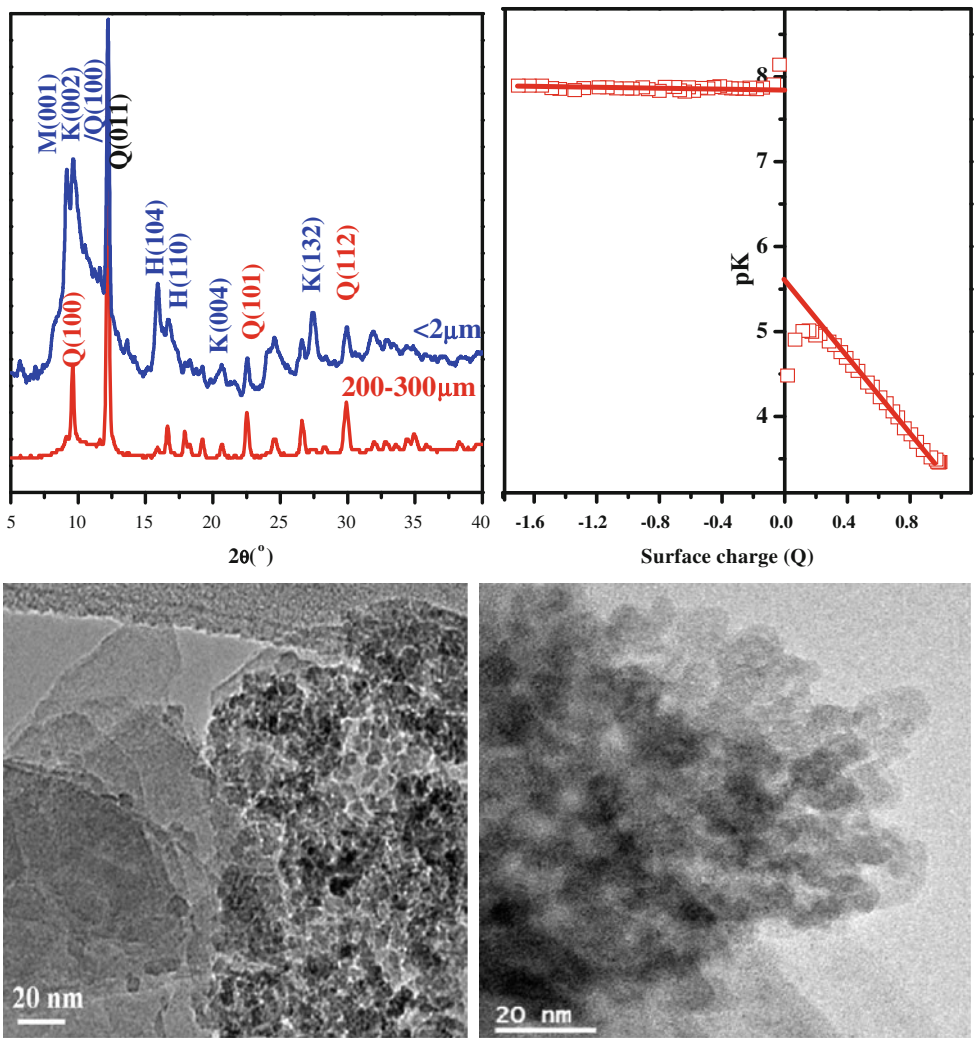

Fig. 2 Characterization of fly ashes. **a** XRD patterns of fly ashes at clay and sand fraction; **b** potentiometric acid–base titration; **c** SEM image before leaching test; **d** SEM image after leaching test by 0.01 mol/L acetic acid

results of XRD pattern at clay fraction. Fly ashes, however, presented severely dissolved after leaching experiments (Fig. 2d). A large amount of metal oxides or hydroxides were dissolved by 0.01 mol/L acetic acid overnight.

pH effect

The $^{64}Cu^{2+}$, $^{63}Ni^{2+}$, $^{60}Co^{2+}$ and UO_2^{2+} leaching from fly ashes as a functional of pH over the wide range 2.0–12.0 were conducted by batch technique. It is found that the amount of radionuclides leaching from fly ashes was significantly decreased with increasing pH. Approximately 5000 μg/kg of $^{64}Cu^{2+}$ was leached from fly ashes, followed $^{63}Ni^{2+}$ (ca. 300 μg/kg), $^{60}Co^{2+}$ (∼60 μg/kg) and UO_2^{2+} (30 μg/kg) at pH 2.0 (Fig. 3).

The ratio of solid to liquid effect

The effect of the ratio of solid-to-liquid (RSL) on radionuclides leaching was also carried out by batch technique (Fig. 4). As shown in Fig. 4, the amount of radionuclides leaching was marked decreased with increasing the RSL from 10.0 to 60.0 g/L. At RSL = 20 g/L, the maximum leaching amount of $^{64}Cu^{2+}$ is found to be ∼5000 μg/kg, which is consistent with the results of $^{64}Cu^{2+}$ leaching at pH 2.0. The leaching amount of radionuclides decreased in the order of $^{64}Cu^{2+} \gg {}^{63}Ni^{2+} > {}^{60}Co^{2+} > UO_2^{2+}$ in terms of RSL-dependent experiments (Table 2).

Particle size effect

According to XRD patterns analysis, the main components of fly ashes varied with particle size. Therefore, it is observed that the different particle size significantly effects the leaching of radionuclides from fly ashes. As shown in Fig. 5, one can see that the amount of $^{64}Cu^{2+}$, $^{63}Ni^{2+}$ and UO_2^{2+} leaching obviously decreases with increasing particle size. The amount of $^{63}Ni^{2+}$ leaching, however, presented dramatically fluctuation with increasing of particle size of fly ashes. It is plausible to assume that the most

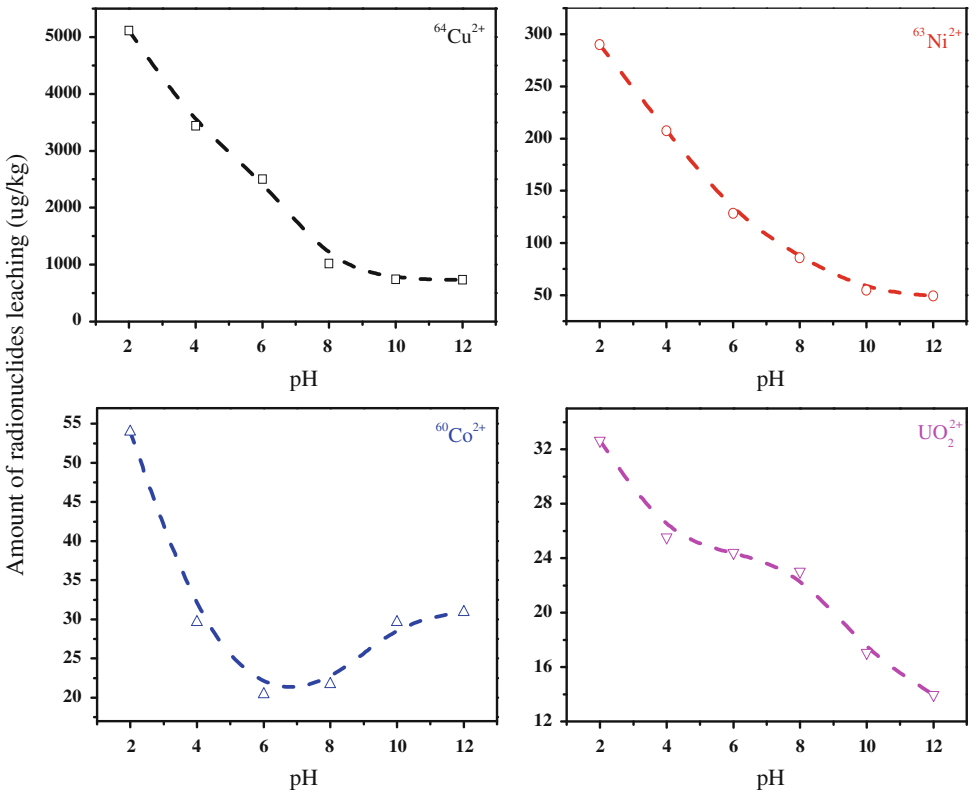

Fig. 3 The effect of pH on radionuclides leaching from fly ashes: the ratio of solid-to-liquid (RSL) = 50 g/L, particle size = 150–200 μm, T = 25 ± 1 °C, *solid lines* are DDLM fit

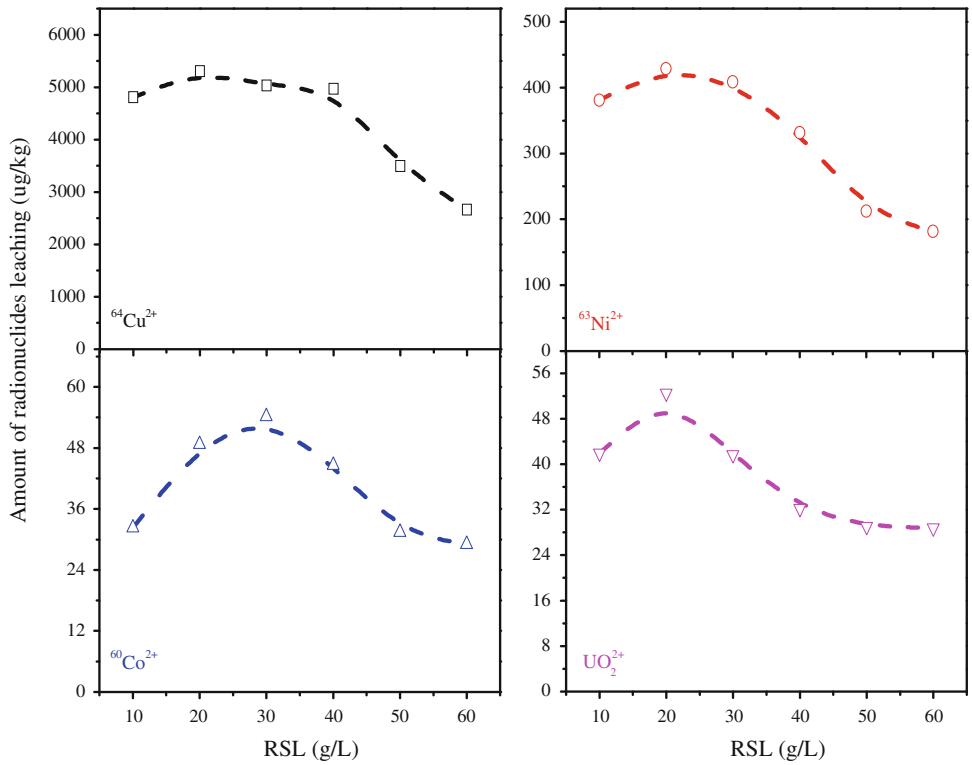

Fig. 4 The effect of ratio of solid-to-liquid (RSL) on radionuclides leaching from fly ashes: pH 4.0, particle size = 150–200 μm, T = 25 ± 1 °C, *solid lines* are DDLM fit

content of $^{64}Cu^{2+}$, $^{63}Ni^{2+}$ and $UO_2{}^{2+}$ focuses on the clay fraction, but clay and sludge fraction dominate the most content of $^{63}Ni^{2+}$ in fly ashes.

Table 2 The surface parameters of fly ashes

Sample	S_{BET} (m^2/g)	Site density (mol/g)	pH_{PZC}
Fly ashes	184.4	4.53×10^{-4}	7.4

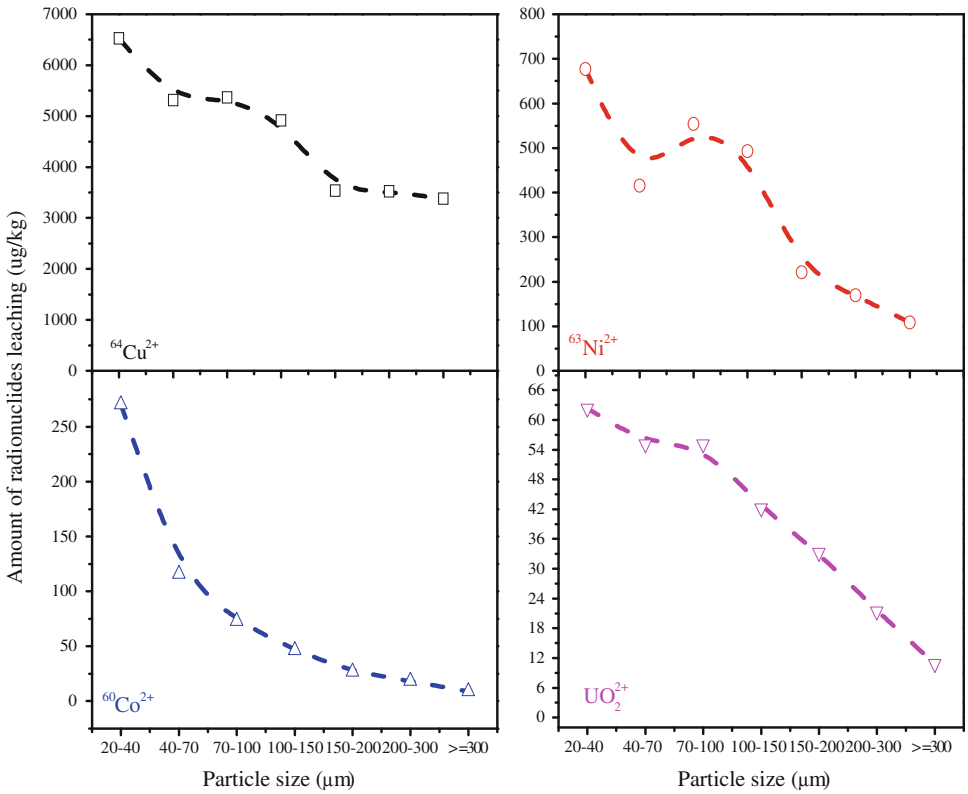

Fig. 5 The effect of particle size on radionuclide leaching from fly ashes: pH 4.0, the ratio of solid-to-liquid (RSL) = 50 g/L, T = 25 ± 1 °C, *solid lines* are DDLM fit

Table 3 The parameters of double layer model for the leaching of radionuclides from fly ashes

Surface reactions	log K			
	$^{64}Cu^{2+}$	$^{63}Ni^{2+}$	$^{60}Co^{2+}$	UO_2^{2+}
$SOH + H^+ = SOH_2^+$	6.3	6.3	6.3	6.3
$SOH = SO^- + H^+$	−8.5	−8.5	−8.5	−8.5
$SOMe^+ + H^+ = SOH^0 + Me^{2+}$	−3.38	−3.77	−4.02	−4.19
$SOMe^+ + H^+ + H_2O = SOH_2^+ + MeOH^+$	−8.28	−8.35	−8.92	−8.96

Application of surface complexation modeling

The highlight of this paper is application of SCM technique on the simulation of $^{60}Co^{2+}$, $^{63}Ni^{2+}$, $^{64}Cu^{2+}$ and UO_2^{2+} leaching from fly ashes. The DDLM technique is employed to simulate the leaching behaviors of radionuclides from fly ashes by using the PHREEQC computer code. As shown in Fig. 3, 4, 5, the leaching behaviors of $^{60}Co^{2+}$, $^{63}Ni^{2+}$, $^{64}Cu^{2+}$ and UO_2^{2+} from fly ashes can be described quite well based on DDLM technique over the whole range of pH values, the ratio of solid-to-liquid and particle size in terms of two surface reactions and corresponding chemical equilibrium parameters (Table 3).

Conclusions

The morphology and surface properties of fly ashes were characterized by XRD, potentiometric acid–base titration and SEM. It is observed that the leaching behaviors of $^{60}Co^{2+}$, $^{63}Ni^{2+}$, $^{64}Cu^{2+}$ and UO_2^{2+} from fly ashes were influenced by environmental factors such as pH, the ratio of solid-to-liquid and particle size. Results of surface complexation modeling showed that the leaching of radionuclides from fly ashes can be well described by DDLM technique.

Acknowledgments Funding for this research was supported from key project of the Natural Science Foundation of Anhui province education office (No. 91126020).

References

1. Zhao L, Zhang F, Wang K, Zhu J (2008) Waste Manage 29:1114
2. Liu Y, Ma L, Liu Y, Kong G (2006) Environ Sci Technol 40: 6411
3. Ibanez R, Andres A, Viguri J, Ortiz I, Irabienm J (2000) J Hazard Mater 79:215

4. Papastefanou C (2008) J Radioanal Nucl Chem 275:29
5. Fisera O, Sebesta F (2010) J Radioanal Nucl Chem 286:713
6. de Carvalho T, Fungaro D, Magdalena C, Cunico P (2011) J Radioanal Nucl Chem 289:617
7. Eighmy T, Eusden J, Krzanowski J, Domingo D, Stampeli D, Martin J, Erickson P (1995) Environ Sci Technol 29:629
8. Rai U, Pandey K, Sinha S, Singh A, Saxena R, Gupta D (2004) Environ Int 30:293
9. McDonald P, Johnston K (1997) J Radioanal Nucl Chem 220:9
10. Hassanein M, EI-Said H, EI-Amir M (2006) J Radioanal Nucl Chem 269:75
11. Hu J, Xu D, Chen L, Wang X (2009) J Radioanal Nucl Chem 279:701
12. Sun Y, Wang Q, Yang S, Sheng G, Guo Z (2011) J Radioanal Nucl Chem 290:643
13. Simsek S, Ulusoy U (2012) J Radioanal Nucl Chem 292:41
14. Zielinski R, Budahn J (1998) Fuel 77:259
15. Karangelos D, Petropoulos N, Anagnostakis M, Hinis E, Simopoulos S (2004) J Environ Radioact 77:233
16. Rahman R, Zaki A (2009) Chem Eng J 155:698
17. Stamberg K, Skrkal J, Benes P, Chalupska K, Vapalka D (1999) J Radioanal Nucl Chem 241:487
18. Gao L, Yang Z, Shi K, Wang X, Guo J, Wu W (2010) J Radioanal Nucl Chem 284:519
19. Hurel C, Marmier N (2010) J Radioanal Nucl Chem 284:225
20. Venkatesan K, Rao P, Stamberg K (2001) J Radioanal Nucl Chem 250:477
21. Chipera S, Bish D (2001) Clays Clay Miner 49:398
22. Dzombak D, Morel F (1990) Wiley, New York
23. Li Y, Xu C, Wei B, Zhang X, Zheng M, Wu D, Ajayan P (2002) Chem Mater 14:483
24. Stumm W, Huang C, Jenkins S (1970) Croat Chem Acta 42:223