



Translocation and toxicity assessment of heavy metals from circulated fluidized-bed combustion of oil shale in Huadian, China

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ABSTRACT

Oil shale and fly ash collected from two thermal power plants located in Huadian, the northeast city of China were subjected to fraction distribution, translocation regularity and toxicity assessment to provide preliminary assessment of suitability for land application. By Tessier sequential extraction, the results showed that Ni, Cr, Pb and Zn were mostly bounded with iron–manganese and organic bound in oil shale, but Cu and Cd were mostly associated with iron–manganese bound and residue fraction. Through circulated fluidized-bed combustion, high concentration of heavy metals (Cu, Cd, Ni, Cr, Pb, and Zn) was found in iron–manganese bound and residue fraction in fly ash. There was accumulation of all studied metals except Ni and Cr in fly ash and translocation mass of metals were as follows: $Pb > Zn > Cu > Cd$ during circulated fluidized-bed combustion. Fly ash was contaminated with Cd higher than the pollution concentration limits listed in GB15168–1995, China. This work demonstrated that it was unadvisable way to carry out landfill without any treatment. By means of STI model, toxicity assessment of heavy metals was carried out to show that there was notable increase in toxicity from oil shale to fly ash.

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1. Introduction

The exploitation of alternative energy sources has attracted more and more attention in the world since a serious decrease of fossil fuels such as coal, petroleum and natural gas due to over-use has been noted. As a possible energy resource substitute, oil shale, which is a natural sedimentary rock with a few of organic matter and rich in ash, has been used to generate electricity and extract oil for several decades [1,2]. In China, more than 5% oil yield is mainly encountered in Huadian of Jilin province, Fushun of Liaoning province and Maoming of Guangdong province [3]. The by-product of oil shale ash is considered as a serious environmental problem [4]. In China, the total annual discharge of oil shale ash is estimated to be more than 800,000 tons. Amount of abandoned oil shale ash have occupied a great deal of cultivated land and have deteriorated environmental quality. Previous studies showed that there was clear accumulation of Pb, Cd, Zn, Tl and As in the fly ash [5]. Taken Maoming city in China for example, the concentration of heavy metals in oil shale ash overran mean values of soil in Guangdong, especially Cu, Zn, Mn, Ni, Pb, Cd and Cr. The discharge of large quantities of heavy metals into water resources has an adverse impact on the environment [6]. The ecological condition deteriorated by abandoned oil shale ash will endanger human health

in different ways, such as the use of polluted surface water and the consumption of any eatable species living in polluted aquatic ecosystem [7].

According to Tessier theory, the heavy metals often occur in five fractions, like exchangeable (EXC), carbonate bound (CAR), iron–manganese bound (Fe–Mn), organic bound (ORG) and residual (RES) fraction, in which the three formers are liable to decompose and others are relatively stable [8]. Because of these, the knowledge of heavy metal content and its fraction in oil shale and fly ash is the most important factors in selecting disposal alternative [9].

Through fluidized-bed combustion, a great quantity of oil shale ash is used to product cement, brick, ceramisite agitator and adsorbent for construction and chemical materials [10–17]. Accompanying with this recycling process, heavy metals are transferred into new products, in which potential toxicity cannot be ignored. When heavy metal content is in superscale, secondary pollution will be caused in industrial application of oil shale ash. Meanwhile, manpower and material resources will be drained. For the thermal and chemical treatment of oil shale ash, the research on heavy metal content and its form will be carried onto provide information for innocent treatment and resource recycling of fly ash.

The present study was carried out to measure the concentration of heavy metals with different fractions in oil shale and oil shale fly ash (OSFA). The main aim of our study is to investigate the distribution regularity and migration mechanism of heavy metal from circulated fluidized-bed combustion of oil shale, and make toxicity

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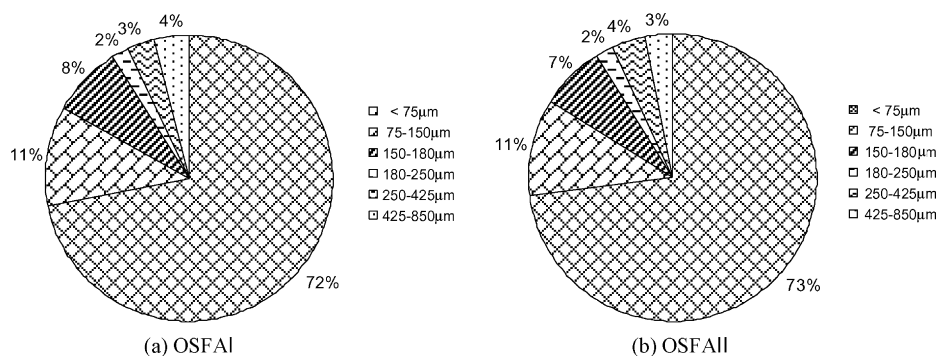


Fig. 1. The particle distribution of OSFA collected from thermal power plants located in Huadian, China.

assessment on OSFA in order to find out whether it is a relatively safe way to product building materials or make landfill without any treatment of OSFA.

2. Materials and methods

2.1. Experimental samples

Oil shale and OSFA in experiment were collected from two thermal power plants of various sizes ranging from 65 to 85 tons per hour located in Huadian, the southeast city of Jilin province, China. Oil shale samples were crushed into particles (<75 µm) to investigate concentration of heavy metals and their fractions, respectively. Through mechanical grading, OSFA was divided into five fractions. As shown in Fig. 1, the mass of fly ash with particles size <75 µm is 4.65 times more than others of size ranging from 75 to 850 µm. For further study on chemical and architectural application, OSFA with particles size <75 µm was selected to measure concentration of heavy metals with different fractions.

2.2. Reagent and apparatus

The extracting solution was prepared from analytical reagents and was checked for possible heavy metal contamination. The analytical reagents in experiments were HNO₃, HClO₄, HCl, MgCl₂, NH₂OH·HCl, NaOAc, NH₄Ac, HOAc and 30% H₂O₂. All reagents matched were performed with deionized water. Glassware used for the experiments was cleaned beforehand with washer solvent by ultrasonic cleaner for more than 20 min and rinsed three times with deionized water.

Apparatus for preparing extractant and separating supernate were given as follows: Leici PHS-25 pH-meter (Shanghai, China), JJ3000 analytical balance (Changshu, China), Sartorius BT 25 S analytical balance (Beijing, China), Guohua SHC-A constant temperature shaker (Changchou, China), Xiangyi L500 centrifugal machine (Changsha, China). The elements concentrations in all supernates were analyzed by Perkin Elmer Analyst 700 atomic absorption photometer (San Diego, USA).

2.3. Extracting methods

Referring to Tessier theory and researches on heavy metal contamination [8,18–20], extracting procedure in this work was given as follows:

Step I: 8 ml solution of MgCl₂ (1 mol L⁻¹, pH 7.0) was added to 1 g of OSFA sample in a 10-ml glass container, continuously shaken for 1 h at 25 °C. The extract was separated from the solid sample by centrifuging at 3000 rpm for 30 min and then the supernate was filtered through 0.45 µm cellulose nitrate filter. The super-

nate was analyzed by Perkin Elmer Analyst 700 atomic absorption photometer. The solid sample was washed with deionized water and underwent next step.

Step II: 8 ml solution of NaOAc (1 mol L⁻¹, pH 5.0) was added to residue from step I in a 10-ml glass container, continuously shaken for 1 h at 25 °C. Other extraction procedure was then performed as described above.

Step III: 20 ml solution of NH₂OH·HCl (0.04 mol L⁻¹) in 25% HOAc (v/v, pH 5.0) was added to residue from step II in a 50-ml glass container, continuously shaken for 6 h at 96 ± 2 °C. Other extraction procedure was then performed as described step I.

Step IV: 3 ml HNO₃ (0.02 mol L⁻¹) and 5 ml 30% H₂O₂ was added to residue from step III in a 50-ml glass container. The mixture was adjusted to pH 2.0 with HNO₃ and shaken occasionally for 2 h at 85 °C. Then, 3 ml 30% H₂O₂ was added to mixture, adjusted to pH 2.0 with HNO₃ and shaken occasionally for 3 h at 85 °C. After cooling, 5 ml NH₄Ac (3.2 mol L⁻¹) was added to mixture, continuously shaken for 0.5 h at 25 °C. Other extraction procedure was then performed as described above.

Step V: 4 ml strong HNO₃ and 1 ml HClO₄ were added to residue from step IV. After digestion of residue, heavy metal concentrations in the supernate were determined as described step I.

2.4. Enrichment factor of heavy metals

Translocation mass of heavy metals from oil shale to OSFA is one of the key components of pollution level. In our study, the mass variation of heavy metals between oil shale and OSFA was described by enrichment factor, calculated according to the following formula:

$$\varepsilon_{ef} = \frac{\sum_{i=1}^n m_{i-FA} - \sum_{i=1}^n m_{i-os}}{\sum_{i=1}^n m_{i-os}} \quad (1)$$

where ε_{ef} is the enrichment factor of heavy metal; m_{i-FA} is the mass of heavy metal with i th fraction in OSFA; m_{i-os} is the mass of heavy metal with i th fraction in oil shale; n is the number of fractions in metal component, according to extraction procedures.

2.5. Statistical analysis

Principal component analysis (SPSS, version 15.0) of heavy metals was calculated based on the correlation matrix, which was performed in different fractions such as EXC, CAR, Fe–Mn, ORG and RES. Principal component analysis was performed for five fractions as variables (EXC, CAR, Fe–Mn, ORG, and RES) to summarize the translocation regularity of heavy metals from oil shale to OSFA. This method produces factors that have high correlation with one smaller set of variables and little or no correlation with another set of variables [8].

3. Toxicity calculation by Synthesis Toxicity Index model

To express concentration of the heavy metals in experimental samples, different models were used to perform toxicity assessment of trace metal mixtures [7,21,22], for example, toxic unit (TU) model, potential ecological risk index (RI) model and Index of Geoaccumulation (Igeo) model. In TU model, toxicity assessment of multimetal pollution is performed by their median effective concentration (EC50), which is 50% concentration of individual metals in mixture [23]. RI model pays more attention to potential ecological risk caused by the total concentrations and toxicity coefficients of heavy metals in mixture. For Igeo model, the total concentrations of heavy metals in mixture have an important effect on pollution level. The calculating methods such as TU, RI and Igeo perform toxicity assessment by virtue of the partial or total concentrations of heavy metals in mixture, which are considered to be pseudo digestion [19]. In fact, the effective concentration of heavy metal which have an impact upon toxicity calculation depends strongly on their specific chemical forms or ways of binding [24]. A rational toxicity assessment model should consider these parameters determining the mobility of trace metals, their bioavailability and related eco-toxicity to plants. In our study, Synthesis Toxicity Index (STI) model was presented to perform the toxicity assessment of present and potential contamination caused by heavy metals with different fractions and quantities [25]. The STI model is expressed as

$$T = \sum_{r=1}^n \left[T_r \left(\sum_{i=1}^m E_i Q_i^r \times 10^{-6} \right) \right] \quad (2)$$

where n is the number of heavy metal components in sample; T_r is the toxicity coefficient of r th metal component in sample; m is the number of fractions in individual metal component, $m=5$ (according to Tessier theory); E_i is the bioavailability coefficient of i th metal form; Q_i^r is the mass of i th form in r th metal component, mg/kg.

According to criterion presented by Lars Hakanson, the toxicity coefficient T_r reflects ecosystem sensitivity to pollution caused by heavy metals (Table 1). Compared with other methods of toxicity assessment, bioavailability pays more attention to influence of heavy metals in different fractions on aquatic ecosystem which plants and animals live in. Previous studies show that bioavailability fraction of metals decreases with time and with increase in pH, clay and organic matter contents [26,27]. In STI model, it is suggested that organic matter have a negligible impact on potential toxicity and pH exert a great influence on valid toxicity of heavy metals. Therefore, the bioavailability coefficient E_i is primarily determined by pH adjusted in each extraction procedure (Table 1). For the resident step, metals extracted are generally considered neither mobile

Table 1
The toxicity coefficient and bioavailability coefficient of heavy metals in STI model.

Heavy metal	T_r
Zn	1
Cu	5
Ni	5
Cr	2
Pb	5
Cd	30
Fractions	E_i
EXC	7.00
CAR	5.00
Fe–Mn	5.00
ORG	2.00
RES	0

nor bioavailable. It is unlike that any naturally occurring processes could dissolve these metals [28]. Consequently, the bioavailability coefficient in resident fraction is defined $E_i = 0$.

4. Results and discussion

4.1. Total concentration of heavy metals in oil shale and OSFA

The concentration of heavy metals with different fractions in oil shale and OSFA were measured by Tessier sequential extraction (Table 2). In the first oil shale sample (OSI), abundance of total heavy metals was followed by Pb, Zn, Ni, Cr, Cu and Cd, whereas in case of the second oil shale sample (OSII) the abundance was as follows: Zn > Pb > Ni > Cr > Cu > Cd. The total concentrations of Pb and Zn were quite higher than those of other metals investigated in experiment. Through circulated fluidized-bed combustion, abundance of total heavy metals in OSFA (OSFAI and OSFAII) was as follows: Pb > Zn > Cu > Ni > Cr > Cd. The total concentrations of Pb and Zn were higher than 250 and 210 $\mu\text{g g}^{-1}$, respectively. Compared with oil shale, there was notable accumulation of Pb, Zn and Cu in OSFA.

4.2. Distribution of heavy metals with different fractions

Many studies on sequential extraction from soils and sewages sludge have usually been carried out to investigate metal mobility and availability [8,20,29]. In this study, the mobility and availability of heavy metals in oil shale and OSFA were studied by their different fractions. As shown in Fig. 2A, the maximum level of Cu, Cd, Pb and Zn in OSI were bound with Fe–Mn, whereas Ni and Cr were found mainly in organic bound. A large quantity of Cr, Pb and Zn in OSII mainly existed in organic bound, while Cd and Ni were mainly bound with Fe–Mn, and Cu was mostly found in residual fraction (Fig. 2B). However, percentages of Pb and Ni with exchangeable fraction in OSFA increased significantly to perform more availability in nature. As shown in Fig. 2, heavy metals (Ni, Cr, Pb, Zn) bounded with ORG were prone to be converted to compounds bounded with

Table 2
Heavy metals extracted from oil shale and OSFA in thermal power plants located in Huadian, China.

Different fractions	Heavy metals ($\mu\text{g g}^{-1}$)					
	Cu	Cd	Ni	Cr	Pb	Zn
OSI						
EXC	2.503	0.340	0.528	1.987	34.621	1.739
CAR	2.347	0.320	1.979	2.167	17.483	9.673
Fe–Mn	6.188	1.299	10.122	7.318	56.012	74.746
ORG	5.566	0.320	13.832	10.788	48.953	67.282
RES	5.618	0.530	1.040	2.539	21.109	14.930
OSII						
EXC	2.762	0.176	1.540	0.588	16.047	2.007
CAR	2.147	0.324	2.399	3.030	16.070	3.446
Fe–Mn	5.717	0.816	15.485	11.543	36.996	47.702
ORG	6.292	0.240	10.893	13.440	49.442	79.169
RES	7.950	0.575	1.285	0.835	16.336	15.131
OSFAI						
EXC	2.319	0.400	3.598	0.983	71.985	1.231
CAR	3.358	0.236	6.533	1.123	20.957	25.586
Fe–Mn	5.798	0.740	8.956	5.777	96.187	105.174
ORG	12.797	0.656	1.403	2.750	51.372	55.257
RES	25.588	1.035	5.432	1.449	15.807	27.615
OSFAII						
EXC	5.078	0.100	3.466	1.059	67.000	1.394
CAR	3.959	0.136	5.477	0.799	18.849	22.433
Fe–Mn	12.795	0.640	4.568	5.467	94.682	113.563
ORG	10.876	0.208	1.559	2.894	59.692	50.129
RES	11.296	1.180	3.503	6.106	11.688	30.996

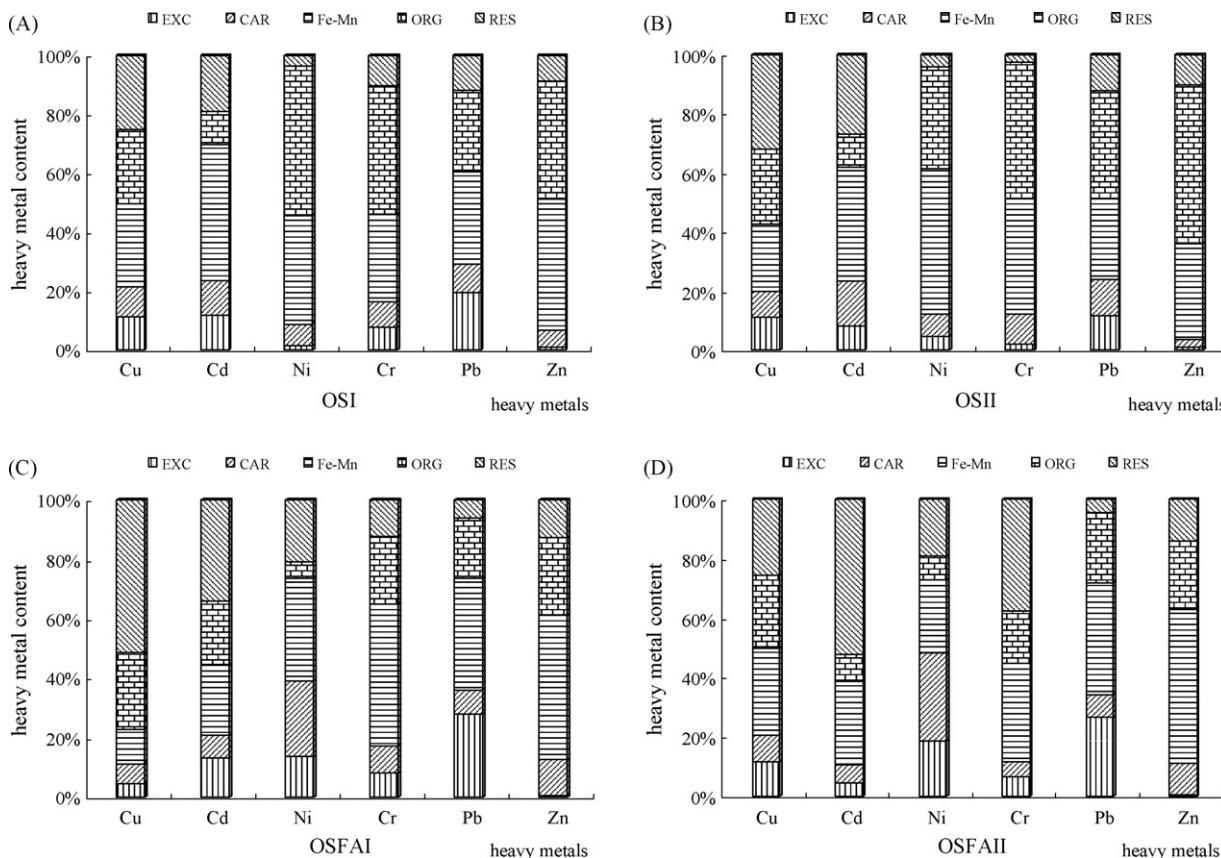


Fig. 2. Chemical speciation of heavy metals investigated on oil shale and OSFA from thermal power plants in Huadian, China.

Fe–Mn and RES due to complicated oxidation reaction in combustion.

Previous studies showed that the elemental contents of fly ash were closed to the melting and boiling points of the elements (metals or compounds) concerned. In general, the lower melting and boiling points for either elements or compounds (oxides, sulfates and chlorides), the higher contents of the corresponding elements in the fly ash [30]. Melting point of metals such as Zn, Cd and Pb and their metal compounds were below the combustion temperature range. It may be supposed that heavy metals in OSFA may originate from the volatilization chlorides and sulfates of Cu, Cd, Ni, Cr, Pb and Zn and their oxides.

4.3. Translocation of heavy metal from oil shale to OSFA

Seen from Table 3, the translocation mass of metals from oil shale to OSFA were as follows: Pb > Zn > Cu > Cd. According to the enrichment factor, the values of translocation mass for all studied metals varied from each other between oil shale and OSFA. After circulated fluidized-bed combustion, there was accumulation of heavy

Table 3 Translocation mass and enrichment factor of heavy metals from oil shale to OSFA.

Metals	OSI–OSFAI			OSII–OSFAII		
	TM ($\mu\text{g g}^{-1}$)	ϵ_{ef}	EL	TM ($\mu\text{g g}^{-1}$)	ϵ_{ef}	EL
Cu	27.630	1.244	***	19.136	0.770	**
Cd	0.257	0.092	*	0.133	0.062	*
Pb	78.130	0.438	**	117.020	0.868	***
Zn	46.493	0.276	**	71.060	0.482	**

*Enrichment level: *minimal ($0 < \epsilon_{ef} < 0.1$); **medium ($0.1 < \epsilon_{ef} < 0.8$); *** maximal ($\epsilon_{ef} > 0.8$).

metals at different level. Accumulation quantity of particular heavy metal ion depends strongly on the melting and boiling point of its chemical compounds. Due to high melting point and boiling point of oxides, there was no accumulation of Ni and Cr in fly ash. Calculated enrichment factor (Table 3) shows that there was notable accumulation of Cu and Pb in OSFA, where the accumulation of other metals was in the order Zn > Cd.

Principle component analysis for heavy metals with different fractions in oil shale and OSFA indicated that two principle components (Fe–Mn and EXC) accounted for 89.60% of the total variance in the complete data set (Fig. 3). This result showed that heavy met-

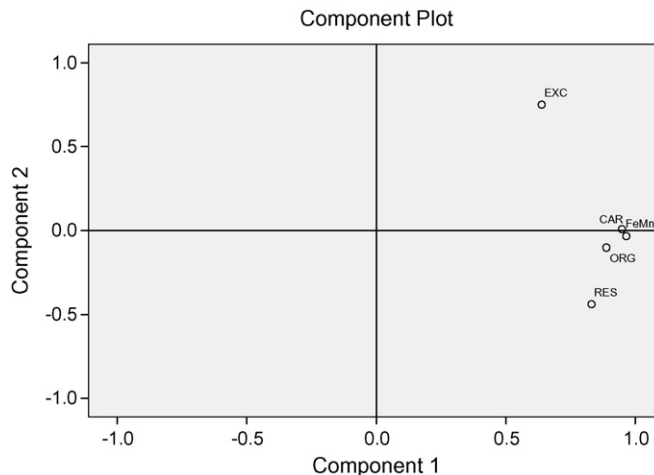


Fig. 3. Principle component analysis of heavy metals with different fractions in oil shale and OSFA.

Table 4
Toxicity assessment of heavy metals on oil shale and OSFA by STI model.

Experiment samples	STI
OSI	0.00542
OSII	0.00394
OSFAI	0.00806
OSFAII	0.00790

als with EXC and Fe–Mn were liable to be generated in oil shale combustion.

4.4. Toxicity assessment of heavy metals on oil shale and OSFA

By means of STI calculation, the toxicity index is significantly enhanced from oil shale to OSFA (Table 4). The main reason is that there was accumulation of heavy metals (Cu, Cd, Pb, and Zn) in OSFA, especially Pb and Zn. In addition, a significant increase in the concentrations of heavy metals with unstable fractions is undoubtedly prone to have an adverse impact on aquatic ecosystem. According to principle component analysis, there were notable accumulations of heavy metals with EXC and Fe–Mn, which led to significant increase in mobility and bioavailability of toxic metals. Among heavy metals in OSFA, Cd exceeded the pollution concentration limits (GB15168–1995, China). Previous studies have identified that accumulation of Cd in human bodies through food chain has caused human health problems, such as renal dysfunction, hypertension, thyroopathy and cancer [31–33]. Therefore, it is apparently showed that environmentalists should pay more and more attention to the danger to aquatic ecosystem and plants around power factory [7]. Because of a potential threat to human health posed by toxic metal ions that enter into biosphere, it was an unadvisable way to carry out industrial application or landfill of OSFA without further treatment.

5. Conclusion

The present study clearly specifies that there were notable accumulation of heavy metals such as Cu, Pb and Zn in OSFA after circulated fluid-bed combustion. Among toxic heavy metals, Cd surpassed the range defined by environmental quality standard for soils of PRC (GB15168–1995). It is necessary that some effective measures should be taken to reduce possible contamination caused by Cd.

Calculated by STI model, the toxicity level of heavy metals in OSFA was significantly enhanced after circulated fluidized-bed combustion. The strong toxicity of heavy metals in OSFA is an obstacle to the direct application without any treatment. The main limitation of this model is that a number of interactions between metals were neglected. Compared with other models, STI model is more useful in carrying out toxicity assessment relating to realistic environment due to consideration of metals with different fractions and quantities.

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References

- [1] M. Hammad, Y. Zurigat, S. Khzai, Z. Hammad, O. Mobydeen, Fluidized bed combustion unit for oil shale, *Energy Conversion and Management* 39 (3–4) (1998) 269–272.
- [2] X.M. Jiang, X.X. Han, Z.G. Cui, Progress and recent utilization trends in combustion of Chinese oil shale, *Progress in Energy and Combustion Science* 33 (6) (2007) 552–579.
- [3] X. Han, X. Jiang, H. Wang, Z. Cui, Study on design of Huadian oil shale-fired circulating fluidized bed boiler, *Fuel Processing Technology* 87 (4) (2006) 289–295.
- [4] R. Shawabkeh, A. Al-Harabsheh, M. Hami, A. Khlaifat, Conversion of oil shale ash into zeolite for cadmium and lead removal from wastewater, *Fuel* 83 (7–8) (2004) 981–985.
- [5] L.A. Aunela-Tapola, F.J. Frandsen, E.K. Hasanen, Trace metal emissions from the Estonian oil shale fired power plant, *Fuel Processing Technology* 57 (1) (1998) 1–24.
- [6] R. Shawabkeh, A. Al-Harabsheh, A. Al-Otoom, Copper and zinc sorption by treated oil shale ash, *Separation and Purification Technology* 40 (3) (2004) 251–257.
- [7] T. Horvat, Z. Vidakovic-Cifrek, V. Orescanin, M. Tkalec, B. Pevalak-Kozlina, Toxicity assessment of heavy metal mixtures by *Lemna minor* L, *Science of the Total Environment* 384 (1–3) (2007) 229–238.
- [8] S. Bose, A. Jain, V. Rai, A.L. Ramanathan, Chemical fractionation and translocation of heavy metals in *Canna indica* L. grown on industrial waste amended soil, *Journal of Hazardous Materials* (2007), doi:10.1016/j.jhazmat.2008.02.19.
- [9] A.A. Zorpas, A.G. Vlyssides, G.A. Zorpas, P.K. Karlis, D. Arapoglou, Impact of thermal treatment on metal in sewage sludge from the Psittalios wastewater treatment plant, Athens, Greece, *Journal of Hazardous Materials* 82 (3) (2001) 291–298.
- [10] X.-P. Feng, X.-L. Niu, X. Bai, X.-M. Liu, H.-H. Sun, Cementing properties of oil shale ash, *Journal of China University of Mining and Technology* 17 (4) (2007) 498–502.
- [11] A.Y. Al-Otoom, Utilization of oil shale in the production of Portland clinker, *Cement and Concrete Composites* 28 (1) (2006) 3–11.
- [12] M.M. Smadi, R.H. Haddad, The use of oil shale ash in Portland cement concrete, *Cement and Concrete Composites* 25 (1) (2003) 43–50.
- [13] C. Freidin, Hydration and strength development of binder based on high-calcium oil shale fly ash, *Cement and Concrete Research* 28 (6) (1998) 829–839.
- [14] A. Kaasik, C. Vohla, R. Motlepe, U. Mander, K. Kirsimae, Hydrated calcareous oil-shale ash as potential filter media for phosphorus removal in constructed wetlands, *Water Research* 42 (4–5) (2008) 1315–1323.
- [15] J. Reinik, I. Heinmaa, J.-P. Mikkola, U. Kirso, Hydrothermal alkaline treatment of oil shale ash for synthesis of tobermorites, *Fuel* 86 (5–6) (2007) 669–676.
- [16] Z. Al-Qodah, A.T. Shawaqfeh, W.K. Lafi, Adsorption of pesticides from aqueous solutions using oil shale ash, *Desalination* 208 (1–3) (2007) 294–305.
- [17] N.R.C. Fernandes Machado, D.M. Malachini Miotto, Synthesis of Na-A and -X zeolites from oil shale ash, *Fuel* 84 (18) (2005) 2289–2294.
- [18] J. Zhang, J. Liu, C. Li, Y. Nie, Y. Jin, Comparison of the fixation of heavy metals in raw material, clinker and mortar using a BCR sequential extraction procedure and NEN7341 test, *Cement and Concrete Research* 38 (5) (2008) 675–680.
- [19] C.M. Davidson, A.L. Duncan, D. Littlejohn, A.M. Ure, L.M. Garden, A critical evaluation of the three-stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially contaminated land, *Analytica Chimica Acta* 363 (1) (1998) 45–55.
- [20] J.W.C. Wong, K. Li, M. Fang, D.C. Su, Toxicity evaluation of sewage sludges in Hong Kong, *Environment International* 27 (5) (2001) 373–380.
- [21] A. Fuentes, M. Llorens, J. Saez, M.I. Aguilar, A.B. Perez-Marin, J.F. Ortuno, V.F. Meseguer, Ecotoxicity, phytotoxicity and extractability of heavy metals from different stabilised sewage sludges, *Environmental Pollution* 143 (2) (2006) 355–360.
- [22] L. Hakanson, An ecological risk index for aquatic pollution control: a sedimentological approach, *Water Research* 14 (8) (1980) 975–1001.
- [23] Y.-J. An, Y.-M. Kim, T.-I. Kwon, S.-W. Jeong, Combined effect of copper, cadmium, and lead upon *Cucumis sativus* growth and bioaccumulation, *Science of the Total Environment* 326 (1–3) (2004) 85–93.
- [24] A. Fuentes, M. Llorens, J. Saez, A. Soler, M.I. Aguilar, J.F. Ortuno, V.F. Meseguer, Simple and sequential extractions of heavy metals from different sewage sludges, *Chemosphere* 54 (8) (2004) 1039–1047.
- [25] A.L. Shujing Liu, Weibo Yuan, Effect of temperature on the heavy metal fraction distribution and comprehensive toxicity on incineration residue of sewage sludge, *Journal of Safety and Environment* 8 (1) (2008) 43–47.
- [26] K. Vig, M. Megharaj, N. Sethunathan, R. Naidu, Bioavailability and toxicity of cadmium to microorganisms and their activities in soil: a review, *Advances in Environmental Research* 8 (1) (2003) 121–135.
- [27] S. Mbarki, N. Labidi, H. Mahmoudi, N. Jedidi, C. Abdely, Contrasting effects of municipal compost on alfalfa growth in clay and in sandy soils: N, P, K, content and heavy metal toxicity, *Bioresource Technology* 99 (15) (2008) 6745–6750.
- [28] J.K. Oygard, E. Gjengedal, H.J. Mobbs, Trace element exposure in the environment from MSW landfill leachate sediments measured by a sequential extraction technique, *Journal of Hazardous Materials* 153 (1–2) (2008) 751–758.
- [29] T. Dekker, G.D. Greve, T.L. Ter Laak, M.E. Boivin, B. Veuger, G. Gortzak, S. Dumfries, S.M.G. Lucker, M.H.S. Kraak, W. Admiraal, H.G. van der Geest, Development and application of a sediment toxicity test using the benthic cladoceran *Chydorus sphaericus*, *Environmental Pollution* 140 (2) (2006) 231–238.
- [30] Y. Zhao, L. Song, G. Li, Chemical stabilization of MSW incinerator fly ashes, *Journal of Hazardous Materials* 95 (1–2) (2002) 47–63.

- [31] Y. Cui, Y.-G. Zhu, R. Zhai, Y. Huang, Y. Qiu, J. Liang, Exposure to metal mixtures and human health impacts in a contaminated area in Nanning, China, *Environment International* 31 (6) (2005) 784–790.
- [32] M. Waisberg, P. Joseph, B. Hale, D. Beyersmann, Molecular and cellular mechanisms of cadmium carcinogenesis, *Toxicology* 192 (2–3) (2003) 95–117.
- [33] M. Castelli, B. Rossi, F. Corsetti, A. Mantovani, G. Spera, C. Lubrano, L. Silvestroni, M. Patriarca, F. Chiodo, A. Menditto, Levels of cadmium and lead in blood: an application of validated methods in a group of patients with endocrine/metabolic disorders from the Rome area, *Microchemical Journal* 79 (1–2) (2005) 349–355.