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Modeling mercury speciation in combustion flue gases using support vector machine: Prediction and evaluation

Bingtao Zhao^{a,*}, Zhongxiao Zhang^a, Jing Jin^a, Wei-Ping Pan^b

^a School of Energy and Power Engineering, University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai 200093, China
^b Institute for Combustion Science and Environmental Technology, West Kentucky University, 2413 Nashville Road, Bowling Green, KY 42101, USA

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ABSTRACT

Mercury emission from coal combustion has become a global environmental problem. In order to accurately reveal the complexly nonlinear relationships between mercury emissions characteristics in flue gas and coal properties as well as operating conditions, an alternative model using support vector machine (SVM) based on dynamically optimized search technique with cross-validation, is proposed to simulate the mercury speciation (elemental, oxidized and particulate) and concentration in flue gases from coal combustion, then the configured SVM model is trained and tested by simulation results. According to predicted accuracy of indicating generalization capability, the model performance is compared and evaluated with the conventional multiple nonlinear regression (MNR) models and the artificial neural network (ANN) models. As a result, it is found that, the SVM provides better prediction performances with the mean squared error of 0.0095 and the correlation coefficient of 0.9164 for testing sample. Moreover, based on the SVM model, the correlativity between coal properties as well as operating condition and mercury chemical form is also analyzed in order to deeply understand mercury emissions characteristics. The result demonstrates that SVM can offer an alternative and powerful approach to model mercury speciation flue gases.

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1. Introduction

Due to the characteristics of volatility, persistence, bioaccumulation and toxicity in the ambient air, mercury pollution can directly give rise to enormous hazards on neurological health [1–9]. In 2005, US EPA issued the Clean Air Mercury Rule (CAMR) [10,11] to permanently cap and reduce mercury emissions from coal-fired power plant for the first time ever. At present, mercury emissions from flue gas by coal combustion have been a global environmental problem. Therefore, it is important to obtain mercury speciation and concentration from combustion flue gases for effective evaluation of mercury emissions and control measurements.

In order to determine mercury speciation in combustion flue gases, it is necessary to develop mathematical models to describe the complicated relationship between mercury emissions and operation conditions of combustion technology. Conventional mathematical models, such as theoretical or semi-empirical models and nonlinear regression method based on statistical analysis, are difficult to directly use for accurate prediction of the mercury emission characteristics in different combustion conditions. Since these models ideally require a very detailed understanding of the mechanisms of mercury transformation, or a very proper correlation for fitting experimental dataset.

In the last two decades, artificial neural network (ANN), as a typical artificial intelligence (AI) model, has been widely applied in the fields of modeling, prediction, fault detection and process control [12]. In the field of mercury pollution control, some ANNs have successfully been applied to predict the mercury speciation in flue gases. Jensen et al. [13] employed a multilayer perceptron (MLP) to estimate the mercury speciation in combustion flue gases. They used the data from 76 power plants to train and develop MLP-ANN. The results showed the estimation of the mercury emissions from selected utility boilers highly agreed with the observed values. Afterward, Adbel-Aal [14] used the GMDH-based abductive ANN for modeling of mercury speciation in flue gases. It was found that a good prediction performance was achieved with the correlation coefficients as high as 0.97 for training data.

With the interdisciplinary development of modern computational technologies and statistical learning theory, support vector machines (SVMs), as new artificial intelligence (AI) model which differs from ANN, has become a more attractive approach for modeling highly complicated and nonlinear system. SVM is a supervised learning theory from the field of machine learning and is applicable for both nonlinear classification called SVMC or SVC and regression called SVMR or SVR. Rooted in the statistical learning theory developed by Vapnik [15] at AT&T, SVM quickly gained attention from

^{*} Corresponding author. Tel.: +86 21 55272740; fax: +86 21 55273704. *E-mail address:* zhaobingtao@usst.edu.cn (B. Zhao).

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many research areas due to a number of theoretical and computational merits, and even marked the beginning of a new era in the learning from examples paradigm [16]. In recent years, SVM has been successfully applied to many fields of pattern recognition, phase diagram assessment, molecular and materials design, trace element analysis, cancer diagnose and chemical engineering and technology, etc. [17]. In the field of mercury emission prediction, unfortunately, SVM so far does not receive a great deal of attention on its algorithmic advantages.

The aim of this work is to obtain a more accurate model based on SVM which is applied to provide a means of predicting mercury speciation emission in combustion flue gases. The estimation performance of this model is comprehensively compared and evaluated with the conventional multiple nonlinear regression (MNR) model as well as different ANN models in the whole study. Further, the effect of coal composition and combustion condition on mercury speciation is also involved based on the prediction results by the present model.

2. Theory

Support vector machines (SVMs) are universal approximator based on statistical and optimizing theory. Originally, SVMs have been developed for classification tasks [18]. With the introduction of Vapnik's ε -insensitive loss function, SVMs have been extended to solve nonlinear regression and time series prediction problems [19–24]. Until now, SVMs have been regarded as powerful methodologies for solving problems in nonlinear classification, density estimation and function estimation.

As reformation to standard SVM, least-square SVM (LS-SVM) [25,26] can be trained much more efficiently after constructing the Lagrangian function by solving the linear Karush–Kuhn–Tucker (KKT) system:

$$\begin{bmatrix} 0 & \vec{1}^T \\ \vec{1} & \Omega + \gamma^{-1}I \end{bmatrix} \begin{bmatrix} b \\ \alpha \end{bmatrix} = \begin{bmatrix} 0 \\ y \end{bmatrix}$$
(1)

According to Mercer's theory [27,28], the relationship between the mapping function and the kernel function was expressed as

$$\Omega_{kl} = \phi(x_k)^I \phi(x_l) = K(x_k, x_l), \quad k, l = 1, ..., N$$
(2)

After arrangement, the LS-SVM regression model can be obtained as

$$\hat{y}(x) = \sum_{k=1}^{n} \alpha_k K(x, x_k) + b \tag{3}$$

where \hat{y} is the estimated output variables, *K* is the kernel function. Commonly, several functions including linear, polynomial, radial basis function (RBF) and multilayer perceptron (MLP) can be used as the kernel function in SVM. Based on the comparison on the availability and adaptability, the RBF function (Gaussian function), Eq. (4), is finally selected as the kernel function due to its good performance under general smoothness assumptions.

$$K(x, x_k) = \exp\left(-\frac{||x - x_k||^2}{\sigma^2}\right)$$
(4)



Fig. 1. Schematic procedure of SVM training and testing.

3. Method

Usually, the SVM modeling procedure can be divided into following steps: selecting variable, dividing sample, optimizing parameters, training and testing simulation and evaluating performance. To more distinctly explain the whole modeling process by SVM theory, the general flow chart of SVM procedure in the present work is illustrated in Fig. 1. All process is carried out on a computer with the hardware configurations: processor, AMD Athlon (TM) 64×2 Dual Core Processor 4400+(2.31 GHz); memory 2.00 GB (DDR2-667 1G \times 2); hard drive, 120 GB (5400 rpm).

3.1. Variable and sample

In coal combustion processes, many factors are responsible for the formation and concentration of mercury. These factors usually include the coal characteristics, operating conditions even the pollutants control technologies. According to the availability of collected data and known mercury correlations, main six associated variables as the input and three chemical forms of mercury as the output are selected as proposed by Jensen et al. [13]. These variables, as shown in Table 1, basically cover the factors which affect the mercury generation and transformation in combustion process, and also used in the SVM model of the present work.

Table 1

Summary of input and output variables for models of the present work.

Input variables	Variable specification	Output variables	Variable specification
X1 X2 X3 X4 X5 X5 X6	Coal heat, Btu/lb, dry Coal Hg, lb/10 ¹² Btu Coal Cl, mass, ppm, dry Coal S, mass%, dry Ash, %, dry Flue gas temperature, °F	\hat{y}_1 \hat{y}_2 \hat{y}_3	Elemental Hg Oxidize Hg Particulate Hg

The 82 samples dataset obtained from the measurements of coal-fired power plant in the USA as part of the Information Collection Request (ICR) scheme in 1998 [29], is used in the present investigation to evaluate the prediction performance of the SVM model. To enhance the reliability of the SVM model, the normalization method and the simple random sampling technique are applied, respectively for the data processing in this work. Due to the large difference in the order of magnitude of the value, the available dataset is transformed or scaled into 0–1 interval using normalization preprocessing method in order to avoid solution divergence, as in Eq. (5). Where x_{Ni} , x_i , x_{min} and x_{max} are the scaled value of the observed variable, actual value of the observed variable, minimum observation value of the dataset, respectively.

$$x_{Ni} = \frac{x_i - x_{\min}}{x_{\max} - x_{\min}} \tag{5}$$

Correspondingly, the final simulation results are also postprocessed by denormalization method in terms of Eq. (5). In addition, to obtain more accurate evaluation of the generalization and robustness performance for the SVM model in the present work, all dataset samples are divided into two non-repetitive groups as the training sample and the testing sample using the simple random sampling (SRS) technique, with the size ratio of 80%:20%.

3.2. Parameters optimization

It is well know that, in SVM model, the key parameters, both the regularization parameter γ and kernel parameter (square of spread factor) σ^2 , play a crucial role in establishing a good SVM regression model with high prediction accuracy and stability. Usually, these parameters are assigned as constants using the semi-empirical correlations. However, it is difficult to decide whether the assigned constant is the optimal value for the SVM model. Therefore, these parameters need to be correctly determined based on the evaluation parameters in order to optimize the prediction performance. For this purpose, a multi-step search (MSS) technique is used in the present work to dynamically seek the optimal values for these key parameters. This technique actually has two steps: first a coarse search and identify a better region in search field according to contour lines of error, then perform a fine search over that region. In process of parameters optimization, the cross-validation is employed to avoid over-fitting. In the present work, The SVM model employs 2D multi-step grid search with 10-fold crossvalidation to seek the optimal hyper-parameters, the regularization parameter γ and the kernel parameter σ^2 . Specifically, the initial values for γ and σ^2 are set as 10 and 0.1, then the optimal search is performed in the interval of (1, 100) and (0.01, 10), respectively. In this stage, the effect of regularization and kernel parameters on 10fold cross-validation error is correspondingly described in Fig. 2. As the figure shows, the symbol in the form of "." represents the results by the first step search. The second step search is performed at minimal cross-validation error by the first step search and is marked with the from of " \times ". Finally, the optimized parameters (γ , σ^2) are obtained at minimal cross-validation error in the second search. Moreover, although there are different cross-validation curved surface for each mercury form, the increase of σ^2 gives rise to significant decrease of the cross-validation error while the change of γ appears to be insensitive to the cross-validation error for all three mercury forms, indicating that σ^2 has predominantly influence compared with γ in the prediction of the mercury speciation.

3.3. Training and testing simulation

Once the optimal values for key parameters are obtained using optimized search technique, the optimized SVM model (the SVM



Fig. 2. Effect of algorithm parameters of SVM on cross-validation MSE for: (a) elemental Hg; (b) oxidized Hg; (c) particulate Hg.

configured with optimized parameters) is trained based on the training data selected at random until it meet the convergence conditions. Subsequently, the trained models are performed to predict the simulated results according to input of the testing data and then compared with the output of testing data. Finally, the model validities are criticized according to the evaluation parameters.

3.4. Evaluation parameters

In order to comprehensively compare the model performance, the evaluation parameters, normalized mean squared error (MSE) E^2 and correlation coefficient (CC) *R* are employed as follows:

$$E^{2} = \frac{1}{n} \sum_{i=1}^{n} (y_{Ni} - \hat{y}_{Ni})^{2}$$
(6)

$$R = \frac{\sum_{i=1}^{n} (y_{Ni} - \bar{y}_{N}) (\hat{y}_{Ni} - \bar{\hat{y}}_{N})}{\sqrt{\sum_{i=1}^{n} (y_{Ni} - \bar{y}_{N})^{2} \sum_{i=1}^{n} (\hat{y}_{Ni} - \bar{\hat{y}}_{N})^{2}}}$$
(7)

Besides, the simulation time (CPU time) *t* is also considered to evaluate the computational efficiency.



Fig. 3. SVM simulation for mercury speciation with optimal parameter (γ , σ^2)=(244.19, 7.41): (a) for training sample and (b) for testing sample.

4. Results and discussion

4.1. Comparison of SVM model with experimental results

The experimental data vs. the configured SVM predictions for mercury speciation are shown in Fig. 3. The solid data points in Fig. 3(a) illustrate the simulation results of mercury speciation by the SVM model for the training samples. According to this figure, it can be seen that all SVM model is able to attain the high training accuracy with the training MSE of 0.0014 and correlation coefficient of 0.9897. To exam the capability of generalization and robustness for SVM model which is emphatically concerned in practical applications, the open data points in Fig. 3(b) describe the simulation results of mercury speciation by the SVM for the testing samples. It is found that the SVM still provides good agreement with the experimental value, with the testing MSE of 0.0095 and correlation coefficient of 0.9164 for the testing stage. It is indicated that, compared with traditional models, the SVM model based on the principle of structural risk minimization and the universal statistical and optimized algorithm has a superior nonlinear fitting capability.

4.2. Comparison of SVM model with MNR model and ANN models

Fig. 4 describes the result calculated by the conventional multiple nonlinear regression (MNR) model which is established using



Fig. 4. MNR simulation for mercury speciation.

the general nonlinear relation with the following appearance:

$$\hat{y} = \alpha_0(x_1^{\alpha_1})(x_2^{\alpha_2})\cdots(x_n^{\alpha_n}) \tag{8}$$

where α_0 to α_n are the equation parameters for the nonlinear relation. Due to complicity of nonlinear relation, Eq. (8) is transformed into the multiple linear regression (MLR) equation to solve the equation parameters. According to the comparison between Figs. 3(b) and 4, it is observed that the MNR model is not satisfactory to give the prediction for all different mercury form, indicating that it is still difficult to accurately model mercury emission behavior through the conventional nonlinear approach because of high complex relationship between coal properties and operating conditions.

In order to evaluate the predicted performance of mercury emissions in combustion flue gases by SVM and artificial neural network (ANN) which belongs to the artificial intelligence model, Fig. 5 describes the generalization performance of the most popular feed-forward neural networks, including back propagation neural network (BPNN), radial basic functions neural network (RBFNN) and generalized regression neural network (GRNN). In this work, all ANNs employ the three layers architecture with a single hidden layer which is able to theoretically approximate a function with the arbitrary accuracy. In these networks, the key parameter, neurons number of hidden layer N_H for BPNN and spread factor also called smoothing parameter σ in the Guassian kernel function for both RBFNN and GRNN, are also determined by the multi-step dynamical search with 10-fold cross-validation. According to the comparison of Figs. 3(b) and 5, the simulation results for testing sample show that the optimized BPNN, RBFNN and GRNN yield the larger prediction error than that of the SVM, although they have the small prediction error for training sample.

In general statistics, the mean squared error (MSE) of an estimator, as a loss function, is one of many ways to quantify the amount by which an estimator differs from the true value of the quantity being estimated. Another parameter, the correlation coefficient (CC) refers to the departure of two random variables from independence. Results with smaller MSW (close to 0) and larger CC (close to \pm 1) indicate that the model can provide the better predicted value to approximate the actual value. According to Figs. 3–5, the testing MSE for mercury prediction by SVM, MNR, BPNN, RBFNN and GRNN is given as 0.0095, 0.1180, 0.0962, 0.0324 and 0.0303, with the correlation coefficient of 0.9164, 0.3310, 0.5278, 0.7107 and 0.7407, respectively. It is indicated that the SVM model presents the best predicted accuracy while the conventional MNR model presents the worst in this case. Moreover, the diagonal isoline in Figs. 3–5 can be



Fig. 5. ANN simulation for mercury speciation: (a) BPNN with the optimal parameter $N_H = 9$, (b) RBFNN with the optimal parameter $\sigma = 0.07$ and (c) GRNN with the optimal parameter $\sigma = 0.34$.

used to intuitively judge the distribution of predicted accuracy. As a whole, the SVM model shows a high predicted accuracy, reliability and uniformity for three kinds of mercury in all concentration level. In comparison, the MNR model only has the reasonable prediction in the low concentration, 0-1 lb/10¹² Btu of coal, but has the underestimate in the high concentration. In the ANN, the BPNN shows the poor robustness in the range of more than 1 lb/10¹² Btu of coal,

especially for elemental mercury and oxidized mercury. The RBFNN and GRNN display the overestimate for particulate mercury and elemental mercury, respectively. In terms of the distribution of predicted results, they are better than MNR model and BPNN model but worse than SVM model. These differences may be attributable to their respective differences in the nature of the model algorithms.

The conventional MNR, as one of most commonly used statistical theory, has the certain advantage in quantitatively analyzing the effects of each input variable on output variable. But compared with the AI models, the MNR must assume the variable distribution, regression function and performed the error check. These will limit its prediction accuracy, even though it has the shortest CPU time (at 0.02 s) in all models in this case. By using the multi-step dynamical search technique with 10-fold cross-validation, the ANN models configuration are able to be effectively improved by overcoming local minima, optimizing spread parameter, etc. However, the BPNN does not display a good generalization performance due to the sensitivity to the initial weight and net structure. In addition, the BPNN has a longest simulation period in terms of the CPU time (at 676.78 s) due to the cycle process of back propagation. Comparatively, by not requiring an iterative procedure the RBFNN and GRNN perform the fast learning speed with the CPU time of 102.21 and 9.36 s, respectively. Nevertheless, the randomicity selecting centre of hidden layer neurons for RBFNN and variable dimensionality for GRNN still partially limits their applicability to give accurate prediction for mercury speciation. Compared with the ANNs, the SVM is from statistical learning theory and has the rigorous mathematical fundamentals. It is a universal approximator based on the principle of structural risk minimization (SRM) and can be transformed into convex optimization problem. These algorithmic characteristics ensure that the SVM can provide the strong generalization capability and guarantee the global optimality in the solution space. At the same time, Compared to the MNR, RBFNN and GRNN, the SVM need to spend much simulation time (at 139.43 s) in two-dimensional grid search and 10-fold cross-validation to obtain two optimal algorithm parameters, γ and σ^2 . However, its computational time is still relatively shorter than that of the BPNN.

4.3. Effect of coal characteristics and operating condition

In practice, it is more concerned to reveal how the mercury emissions in different forms are related to coal property and combustion conditions. Due to strong robustness and generalization performance, it is feasible that the SVM model can be used to determine this relationship. For this purpose, the correlations of individual input variable (heat value, total mercury, chlorine, sulfur and ash as well as flue gas temperature) with output variable (elemental Hg, oxidized Hg and particulate Hg) are given by the configured SVM model in the different disturbance amplitude, as shown in Table 2 and Fig. 6. In this stage, the full dataset sample is trained and simulated in order to obtain the more comprehensive and accurate results.

As can be seen from Table 2, it is observed that all correlation coefficients are nonzero values which show the reasonable relationship exists between 6 selected input variables and 3 output variables. Moreover, in the range of $\pm 20\%$, it can also be observed that the correlation coefficients for each input variable do not have the significant variance, indicating that SVM model can provide the sufficient stability and reliability and can be used for mercury emission prediction and estimation.

According to Fig. 6, it is also found that in the given experimental samples, the influence of individual explanatory variable on mercury physicochemical form exhibits as complex mapping relationship. The coal heat shows the negative correlation with elemental mercury and the absolute value of mean correlation coefficient is greater than that of both oxidized and particulate

(Correlation coefficient between coal properties as well as operating condition and mercury speciation with different disturbance amplitude.															
		DA=-20%		DA=-10%		DA=0%		DA=10%			DA=20%					
		EM	ОМ	PM	EM	OM	PM									
	Н	-0.3247	0.1336	0.3007	-0.3190	0.1682	0.2824	-0.3141	0.1522	0.2777	-0.3110	0.0932	0.2870	-0.3081	0.0290	0.3075
	М	0.5489	0.5663	0.0983	0.5271	0.5915	0.0884	0.5124	0.6132	0.0842	0.5041	0.6252	0.0871	0.4996	0.6309	0.0976
	С	-0.1572	0.2720	0.4647	-0.1831	0.2731	0.4780	-0.1904	0.2877	0.4754	-0.1776	0.3067	0.4523	-0.1517	0.3194	0.4164
	S	-0.1075	0.4834	0.1540	-0.1353	0.5873	0.1069	-0.1490	0.6249	0.0839	-0.1405	0.5802	0.0956	-0.1170	0.4938	0.1291
	А	-0.0347	0.2282	0.1503	-0.0864	0.1808	0.1557	-0.1233	0.1040	0.1651	-0.1435	0.0258	0.1812	-0.1491	-0.0254	0.2011
	Т	0.4732	0.3122	-0.2738	0.5331	0.2949	-0.3238	0.5713	0.2644	-0.3467	0.5904	0.2309	-0.3437	0.5919	0.2099	-0.3190

 Table 2

 Correlation coefficient between coal properties as well as operating condition and mercury speciation with different disturbance and

DA = disturbance amplitude; EM = elemental mercury; OM = oxidized mercury; PM = particulate mercury. H = heating value of coal; M = mercury in coal; C = chloride in coal; S = sulfur in coal; A = ash in coal; T = temperature of flue gas.

mercury, suggesting that the increasing coal heat value decreases the elemental mercury emission whereas increase the oxidized and particulate mercury emission. The positive correlation between the coal mercury and both the elemental and oxidized mercury is demonstrated, with the mean correlation coefficient of 0.5184 and 0.6054, respectively. It is inferred that in the combustion environment, the mercury from coal is mostly transformed as gaseous mercury in the form of Hg⁰, Hg⁺ (CH₃Hg, HgCl, etc.) and Hg²⁺ (HgCl₂, HgO, HgSO₄, HgS and Hg(NO₃)₂, etc.), and appears to have not directly large contribution to particulate mercury (mean correlation coefficient of 0.0911). The chlorine and sulfur from coal are found to be the two impact factors of gaseous mercury emissions. They present the similar effect on elemental mercury with the coefficient of -0.1720 and -0.1299 as well as on oxidized mercury with the coefficient of 0.2918 and 0.5539, respectively. Actually, the effect is mainly attributed to the intermediate products, HCl and SO₂, which generated from chlorine and sulfur in coal combustion process [30], and help to promote the elemental mercury oxidation reaction. In addition, the chlorine content of the coal is favorable to transformation from the gaseous to the particulate mercury [31]. As a result, the particulate mercury obtains quickly accumulation and has a high emission concentration with the mean correlation coefficient of 0.4574. Compared with other explanatory variables, the ash of coal displays low correlation for elemental and oxidized mercury emission. Even so, the increasing coal ash still gives rise to the decrease of the elemental mercury and the increase of particulate mercury. On the one hand, the fly ash from coal ash in flue gas can inhibit the mercury oxidization. On the other hand, the increasing fly ash content not only enhances its adsorption capability to gaseous mercury, but also affects the equilibrium ratio between the gaseous and particulate mercury [32,33]. Based on the effect of flue gas temperature, it can be extrapolated that the elemental mercury is difficult to proceed with the oxidized reaction in high flue



Fig. 6. Mean correlation coefficient between coal properties as well as operating condition and mercury speciation.

gas temperature which leads to the increase of elemental mercury. Simultaneously, due to negative influence of the temperature on the adsorption equilibrium, high flue gas temperature reduce the adsorption capability of the fly ash particles to gaseous mercury which results in the rapid reduction for the particulate mercury, with the mean correlation coefficient of -0.3214.

Finally, it is also necessary to note that, for the SVM model used to predict the mercury speciation, the correlation coefficient between the input and output variable in Table 2 is only valid for a single input variable changed while keep other input variables unchanged as well as all input variables must be independent. Actually, the input variables for the SVM model may not be absolutely or completely independent in this case, e.g., in the combustion process, heat value of coal sometimes directly affects the flue gas temperature and is indirectly related with the release characteristics of Hg, Cl, S and ash in coal. In order to overcome this situation, the selection of the input variables needs to be more representative and independent. Although the SVM algorithm may not be limited by the independence of input variable, a high degree of independence of input variable can significantly enhance the generalization capability and prediction accuracy of the model, and, may sometimes be effective to reduce the dimension of sample space.

5. Conclusions

Support vector machine (SVM) is demonstrated as a powerful and alternative approach to model mercury speciation in the flue gases from coal combustion. By using SVM it is helpful to estimate emission characteristics of mercury speciation and develop control technologies for mercury pollution.

Although the SVM need to spend much CPU time for implementation than that of MNR and other ANN models except for the BPNN model, it still has at least 69% reduction in prediction error for the testing sample in this case, indicating that SVM is able to successfully correlate the mercury speciation with coal properties and operating temperature, and provide the superior performance on the precision and stability of mercury speciation prediction with the high generalization and robustness capability. Further, it is still necessary to develop the high-performance artificial intelligence models and advanced optimal search algorithm in order to make more accurate and high efficient prediction for mercury speciation.

Although SVM model can be used to analyze the correlativity between coal properties (heating value, total mercury, chloride, sulfur and ash) as well as operating condition (flue gas temperature) and mercury speciation with different chemical form (elemental, oxidized and particulate mercury), it does not take into account the effects of the combustion conditions (e.g., excess air, nitrogen oxide and fly ash characteristic), the combustion mode and the air pollution control devices (e.g., particulate collector, FGD leading to mercury re-emission and SCR enhancing mercury oxidation). Obviously, it might be anticipated that the prediction performance of SVM should be improved if the explanatory variables include these associated impact factor.

- References
- J.H. Pavlish, E.A. Sondreal, M.D. Mann, E.S. Olson, K.C. Galbreath, D.L. Laudal, S.A. Benson, Status reviews of mercury control options for coal-fired power plants, Fuel Processing Technology 82 (2003) 89–165.
- [2] R. Yan, D.T. Liang, L. Tsen, Y.P. Wong, Y.K. Lee, Bench-scale experimental evaluation of carbon performance on mercury vapor adsorption, Fuel 83 (2004) 2401–2409.
- [3] H. Zeng, F. Jin, J. Guo, Removal of elemental mercury from coal combustion flue gas by chloride-impregnated activated carbon, Fuel 83 (2004) 143–146.
- [4] W.J. O'Dowd, R.A. Hargis, E.J. Granite, H.W. Pennline, Recent advances in mercury removal technology at the national energy technology laboratory, Fuel Processing Technology 85 (2004) 533–548.
- [5] W.J. O'Dowd, H.W. Pennline, M.C. Freeman, E.J. Granite, R.A. Hargis, C.J. Lacher, A. Karash, A technology to control mercury from flue gas: the thief process, Fuel Processing and Technology 87 (2006) 1071–1084.
- [6] M. Diaz-Somoano, S. Unterberger, K.R.G. Hein, Mercury emission control in coal-fired plant: the role of wet scrubbers, Fuel Processing Technology 88 (2007) 259–263.
- [7] P. Li, X.B. Feng, G.L. Qiu, L.H. Shang, Z.G. Li, Mercury pollution in Asia: a review of the contaminated sites, Journal of Hazardous Materials 168 (2009) 591–601.
- [8] J.W. Graydon, X. Zhang, D.W. Kirk, C.Q. Jia, Sorption and stability of mercury on activated carbon for emission control, Journal of Hazardous Materials 168 (2009) 978–982.
- [9] Y. Chi, N.Q. Yan, Z. Qu, S. Qiao, J. Jia, The performance of iodine on the removal of elemental mercury from the simulated coal-fired flue gas, Journal of Hazardous Materials 166 (2009) 776–781.
- [10] U.S. EPA, Regulatory Impact Analysis of the Final Clean Air Mercury Rule, Office of Air Quality Planning and Standards, EPA 452/R-05-003, March 2005.
- [11] J.L. Ren, J.S. Zhou, Z.Y. Luo, Y.J. Zhong, K.F. Cen, Mathematical modeling of mercury removal from simulated flue gases, Journal of Zhejiang University 40 (2006) 1827–1832 (in Chinese).
- [12] J.L. Dirion, B. Ettedgui, M. Cabassud, M.V. Le Lann, G. Casamatta, Elaboration of a neural network system for semibatch reactor temperature control: an experimental study, Chemical Engineering and Processing 35 (1996) 225–234.
- [13] R.R. Jensen, S. Karki, H. Salehfar, Artificial neural network-based estimation of mercury speciation in combustion flue gases, Fuel Processing Technology 85 (2004) 451–462.
- [14] R.E. Abdel-Aal, Predictive modeling of mercury speciation in combustion flue gases using GMDH-based abductive networks, Fuel Processing Technology 88 (5) (2007) 483–491.
- [15] V.N. Vapnik, The Nature of Statistical Learning Theory, Springer-Verlag, New York, 1995.

- [16] L. Jin, P. Nikiforuk, M. Gupta, Direct adaptive output tracking control using multilayered neural networks, IEEE Proceedings-D 140 (6) (1993) 393–398.
- [17] N. Chen, W. Lu, J. Yang, G. Li, Support Vector Machine in Chemistry, World Scientific Publishing Company, 2004.
- [18] M. Schmidt, Identifying speaker with support vector networks, in: Interface 96 Proceedings, Sydney, 1996.
- [19] V.N. Vapnik, S.E. Golowich, A.J. Smola, Support vector method for function approximation, regression estimation, and signal processing, Advances in Neural Information Processing Systems 9 (1996) 281–287.
- [20] V.N. Vapnik, An overview of statistical learning theory, IEEE Transaction of Neural Networks 10 (5) (1999) 988–999.
- [21] A.J. Smola, Learning with kernels, PhD Thesis, GMD, Birlinghoven, Germany, 1998.
- [22] K.R. Muller, J.A. Smola, G. Ratsch, B. Scholkopf, J. Kohlmorgen, Prediction time series with support vector machines, in: Advances in Kernel Methods, The MIT Press, London, England, 1999.
- [23] F.E.H. Tay, L.J. Cao, e-Descending support vector machines for financial time series forecasting, Neural Processing Letters 15 (2002) 179–195.
- [24] L.J. Cao, H.P. Lee, C.K. Seng, Q. Gu, Saliency analysis of support vector machines for gene selection in tissue classification, Neural Computing & Applications 11 (3-4) (2003) 244-249.
- [25] J.A.K. Suykens, J. Vandewalle, Least squares support vector machine classifiers, Neural Processing Letters 9 (3) (1999) 293–300.
- [26] J.A.K. Suykens, J. Vandewalle, B. De Moor, Optimal control by least squares support vector machines, Neural Networks 14 (1) (2001) 23–35.
- [27] T. Mercer, Functions of positive and negative type and their connection with the theory of integral equations, Philosophical Transaction of the Royalty Society of London, Series A (1909) 415–446.
- [28] V.N. Vapnik, S. Golowich, A. Smola, Support Vector Method for Function Approximation, Regression Estimation and Signal Processing, Advances in Neural Information Processing Systems, vol. 9, MIT Press, Cambridge, MA, 1997.
- [29] U.S. Environmental Protection Agency Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990–1999, EPA 236-R-01-001, United States Environmental Protection Agency, April 2001.
- [30] S. Kellie, Y. Cao, Y.F. Duan, L.C. Li, P. Chu, A. Mehta, R. Carty, J.T. Riley, W.P. Pan, Factors affecting mercury speciation in a 100-MW coal-fired boiler with low-NO_x burners, Energy & Fuels 19 (2005) 800–806.
- [31] C.X. Hu, J.S. Zhou, J.M. Zheng, Z.Y. Luo, K.F. Cen, Influence of chlorine and ash on flue gas mercury speciation of large scale coal-fired boilers, Chinese Journal of Power Engineering 28 (6) (2008) 945–948 (in Chinese).
- [32] C.J. Wu, Y.F. Duan, C.S. Zhao, Adsorption characterization of mercury by fly ashes during co-combustion of sludge and coal, Proceedings of the Chinese Society for Electrical Engineering 28 (14) (2006) 55–59 (in Chinese).
- [33] Z. Li, X. Sun, J. Luo, J.Y. Hwang, Unburned carbon from fly ash for mercury adsorption. II. Adsorption isotherms and mechanisms, Journal of Minerals & Materials Characterization & Engineering 1 (2) (2002) 79–96.