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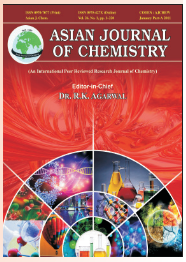

Studies on Capture of Modified Ca-Based Sorbents for Zn, Pb, As in Coal During the Process of Combustion Based on the Analysis of Fundamental Characteristics of Trace Elements and Coal Samples†

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This paper systematically expounds the fundamental characteristics of trace elements (zinc, lead, arsenic) in the coal samples, including content, occurrence, phases, microstructure, morphology and melting properties by the analysis of AFS, XRD, SEM-EDX and TG-DSC. It also discusses the thermodynamic behaviour and the mechanisms of migration and transformation on the basis of the experimental phenomena and the analyzed information. The capture efficiencies of the modified Ca-based sorbents (MCS) for Zn, Pb, As were studied comparative to the experimental results of calcium carbonate. The content of Zn, Pb and As in the coal samples were nearly all exceeding the standard values. Zn and Pb occurred mainly in the form of exchangeable, bound-sulfide and residue in the coal samples and more than 50 % of As was bound-sulfide. Zn, Pb and As in the most coal samples evaporated and gasified following the priority of As > Zn > Pb during the process of coal static combustion experiment. The lowest volatilization rate of Zn, Pb and As with the addition of modified Ca-based sorbents were18.81, 14.44 and 26.13 %, respectively under the optimal experimental condition, which were much lower than the ratio with calcium carbonate under the same experimental condition. The surface area, pore diameter and porosity of calcium carbonate modified by $Al_2(SO_4)_3$ were obviously improved, some γ-Al_2O_3 was found on the surface of the particle and the melting temperature of the coal mixed with modified Ca-based sorbent was high.

Keywords: Coal combustion, Trace elements, Migration and transformation, Modified Ca-based sorbent, Volatilization rate.

INTRODUCTION

Coal is one of the important energy sources which will be continuously and broadly used in this century due to its predictably abundant reserves and the reserves of the coal in China are about 1.5 trillion tons[1,2]. Nearly 76 % of power plants, 75 % of industrial production, 80 % of residential accommodation and 60 % of chemical enterprises are powered by the consumption of coal. Coal contains almost all the elements presented in the periodic table[3,4]. The geochemical evolution of coal deposits resulted in many trace elements being enriched in coal with extensive concentration ranges which are totally affected by the change of both region and environment[4]. Some trace elements (TEs) emitted during coal combustion have high impacts on the environment and present potential health problems for the human[2]. Previous studies on the control of heavy metals have indicated that it is difficult to control the volatilization of metals during high temperature processes[5,6]. So, it is important to know the total content and mode of occurrence and XRD pattern of each element in coal. The distribution, mobility and bioavailability of trace elements depend not only on their total concentration, but also on their associated occurrences and speciation distribution. Trace elements' distribution in coal is crucial since it promotes and accelerates the possible prediction of mechanisms of release from combustion[7-10] and health risk caused by the release of some specific trace elements is more closely related to the speciation than the total content[11,12].

During the process of coal combustion, most of the trace elements are partially or fully gasified and vaporized. The metallic vaporization/evaporation condense and enrich in the submicron particles when the temperature gradually decreases[13-15]. The air pollution control devices (APCDS) such as wet scrubbers, bag-house, electrostatic precipitator and cyclones are traditionally used to collect the particulates formed by thermal decomposition of coal during the process

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of the combustion. However, the capture efficiency is very low due to the huge differences in some facts, including the direct gaseous emission of several volatile trace elements, the size-distribution in fly ashes their enrichment in the submicron particles and the formation and transformation of fly ash particles[16]. Capture of these species on solid sorbents by both physical deposition and chemical reactions is an alternative control method. The emission of heavy metals can be effectively inhibited by blending the solid sorbents into coal or injecting semi-dry sorbents into the flue during incineration processes. Compositions and occurrences of trace elements and types of sorbents mainly affect the capture efficiency of the sorbents for some heavy metal compounds. The interaction between trace metals and various sorbents have been widely and extensively studied by many researchers[17-20] based on three mechanisms in capturing trace elements during coal combustion and incineration, metallic ash capture, vapour capture and particulate capture[21,22]. In terms of all kinds of sorbents, Si-, Al- and Ca-based sorbents are found to be more efficient in capturing metals during incineration and combustion processes[23-26]. In this paper, to strengthen and enhance the capture ability of traditional Ca-based sorbents, aluminum sulfate [$Al_2(SO_4)_2$], the quantitative sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3) were input to the coal samples. Aluminum sulfate was poured into the coal samples for combined utilization and the quantitative sodium carbonate and potassium carbonate were input to further improve the surface area, distribution of the pore diameter and porosity of the sorbent in the process of modulation of MCS, based on the analysis results of fundamental characteristic features of trace elements (Zn, Pb, As) in the coal samples.

EXPERIMENTAL

Collection and preparation of coal samples: There are huge difference existed between the content of the different trace elements in the different coal samples based on the product of the earth and chemical evolution. They are mainly linked with the ancient environment of the coal swamps and the diagenetic process of coal bed[27,28]. The content of heavy metals are also associated with regional geography and organic matter and diagenetic minerals are the main carriers for most of trace elements. There were seven coal samples which came from SongZao (Chongqing, 1#) mine, LinHua and LiuPanShui (Guizhou, 2# and 8#) mines, XiShan and WuYang (Shanxi, 3# and 4#) mines, XieYi (Anhui, 5#) mine, Cina (Yunnan, 6#) mine and HuaYing mine (SiChuan, 7#) in China, were prepared for the experiment. The coal samples were grounded into fine particles (< 0.2 mm) and then carefully sifted through a 200-mesh sieve after being naturally air-dried which is referred from the national standard GB474-2008.

Preparation of modified Ca-based sorbent: Modified Ca-based sorbent was modulated by the process of chemical impregnation, which produce homogeneous materials. Weighing grams of calcium carbonate, $Al_2(SO_4)_3$, Na_2CO_3 and K_2CO_3 separately according to a set number of ion ratios (γ, Ca^{2+}/Al^{3+}, K^+, Na^+, mol/mol), adding water and stir evenly 2 h with a glass rod under the condition of the uniform heating (water bath) and constant temperature (95 ºC). After then, the mixture was filtered separately, dried in the constant temperature drying box and sieved into 200-mesh. Alumina corundum crucible was going to be used during coal combustion in order to avoid the chemical reactions between alkali metal salt and the frequently-used silica ceramic crucible.

General procedure and detection method

Total content and occurrence characteristics of Zn, Pb and As in coal samples: In order to obtain the total content of trace elements in coal, 5 mL of HNO_3, 2 mL of H_2O_2 (30 %) and 3 mL HF were added to 0.2 g samples. The solid was digested in the Microwave Digestion System (MD6). After cooling and filtration, obtained liquid was diluted to 100 mL with deionized water and was measured by atomic fluorescence spectrometer (SK-2002B)[29]. The content of the combustion/incineration residue (A_{ad}) has a potential significance to explore the migration and transformation of heavy metal elements in coal and A_{ad} were obtained by the reference of the national standard GB212-91 (China) in the experiment. The speciation study was carried out with sequential extraction and four fractions: exchangeable (F1), bound to sulfide (F2), bound to organic matter (F3) and residue (F4) were accepted and abided. The concentration of the ordinal solutions of F1, F2 and F3 were measured by atomic fluorescence spectrometer (SK-2002B) and the content of the trace elements in F4 were gotten through calculating the difference between the total content and the sum of F1, F2 and F3[30].

Mineral phases and melting characteristics analysis of the coal samples: The coal samples were dried at room temperature and sieved to 200-mesh and then were evenly sprayed on the surface of the rounded glass plate (diameter, 1 cm, thin, 2 mm) with conductive adhesive. The plate were finally sprayed with gold and placed into the equipment (Shimadzu XRD-6000) with labeled numbers. The MDI Jade 5.0 (software) was introduced to calculate and provide the diffraction pattern. When the melting temperature is low, the burning of the coal is usually not sufficient, which can increase the carbon content in ash and cause the slagging. A large amount of slags may clog the grate, cause discharge difficulty and even cause an accident of furnace. In addition, the phenomenon of the corrosion on the lining refractories will happen when the acid-base property between the slag and lining bricks does not match well[31]. Thus, it is necessary to study the effect of MCS on the melting characteristics of coal ash. The synchronous thermal analyzer (NET2SCH/STA 449C) was used to analyze the melting features of the coal and calculate the raw data according to the design of national standard GB212-91. The highest temperature is 1450 ºC, heating rate is 20 ºC/min and the measurement atmosphere is oxidizing.

Microstructure and surface morphology of $CaCO_3$ and modified Ca-based sorbent: The main parameters for the microcosmic structures of sorbents, specific surface area, porosity and pore diameter distribution have a high impact on the reaction rate and diffusion of trace elements in coal during the process of combustion. The microstructures of $CaCO_3$ and MCS were analyzed with the help of ASAP2010 analyzer in the experiment. The morphology of MCS was characterized using scanning electron microscopy with emission spectrometry analysis (SEM-EDX).

RESULTS AND DISCUSSION

Content of Zn, Pb, As in the coal and XRD pattern: There is no unified standard on the harm to the environment based on the content of heavy metals in the raw coal, so it is difficult to quantitatively evaluate its level. In this paper, the average content of trace elements in coal, in China is used as an evaluation standard, which is reported by the Chinese scholars by collecting, sorting data of the content of related elements in more than 1529 coal samples[32]. The experimental results of the content of Pb, As and Zn are listed in Table-1. It can be found that the content of the same element in the different coal samples was entirely different and the difference of the distribution was very apparent. The content of Zn, Pb and As in the most coal samples were more than or close to the average and were lower than the values of environmental quality standard for soils (GB15618-2008). The attention should be paid to considering the features of trace elements' migration to the environment, feasibility, concealment and bioaccumulation and the usage amount each year.

TABLE-1
TOTAL CONTENT OF THE HEAVY METALS IN RAW COAL (μg/g)

Coal sample	Zn	As	Pb
1#	34.05	4.74	20.73
2#	35.72	5.06	23.36
3#	13.49	0.81	21.52
4#	28.13	4.40	17.68
5#	26.68	2.87	9.49
6#	41.10	9.03	19.43
7#	58.06	14.58	25.68
8#	32.13	8.12	15.58
Average content of trace elements in China	38	5	14
GB15618-2008	500	50	300

Fig. 1 showed XRD pattern of the coal samples (1#, 2#). The MDI Jade 5.0 (software) was introduced to calculate and provide the diffraction pattern. The data of the X-ray diffraction spectrogram and the PDF cards of material libraries (database of inorganic materials, minerals, ICSD inorganic materials and ICSD minerals) were input into the software before the research and the retrieval. After the end of the retrieval, the major phases and fom (the reciprocal of matching rate) of the correspondent (major phases) were displayed from small to large order. Some smaller intensity peaks which cannot be detected and retrieved by the software need to be searched by hand. The coal samples contain several kinds of major mineral phases, including quartz, kaolinite, pyrite, anatase, silicate, clinochlore and nitrite. Zinc is in the forms of zinc chlorate [$Zn(ClO_3)_2$], sphalerite (ZnS), zinc oxide (ZnO) and zinc silicate (Zn_2SiO_4). Lead is in the forms of lead phosphate [$Pb_3(PO_4)_2$], lead oxide nitrate [$Pb_4(NO_3)_2O_3$], lead arsenate ($PbAs_2O_6$) and lead silicate (Pb_3SiO_5). The arsenic is in the form of claudetite (As_2O_3), arsenic oxide chloride ($As_4O_5Cl_2$), duranusite (As_4S) and lead arsenate ($PbAs_2O_6$).

Sequential extraction and speciation distribution of Zn, Pb and As in coal: Sequential extraction procedures and the high-pressure digestion method were selected to determine the element constituents of coal samples and occurrence characteristics of trace elements. Figs. 2-4 have listed the speciation distributions of Zn, Pb and As in the coal samples. Exchangeable (F1) means mobile and bioavailable, the higher of this fraction the more danger to the environmental system and health of person. Bound to sulfide (F2) and bound to organic (F3)

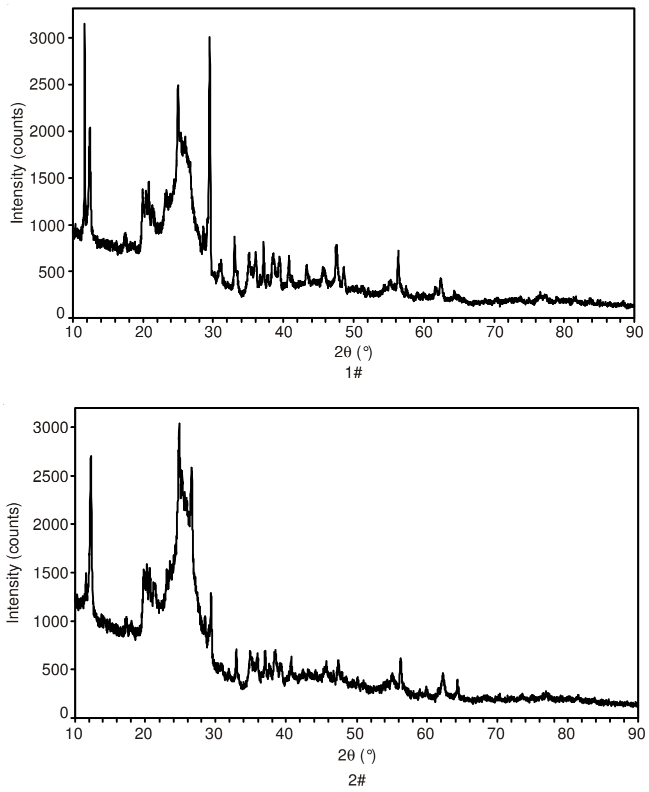

Fig. 1. XRD pattern of the coal samples (1# and 2#)

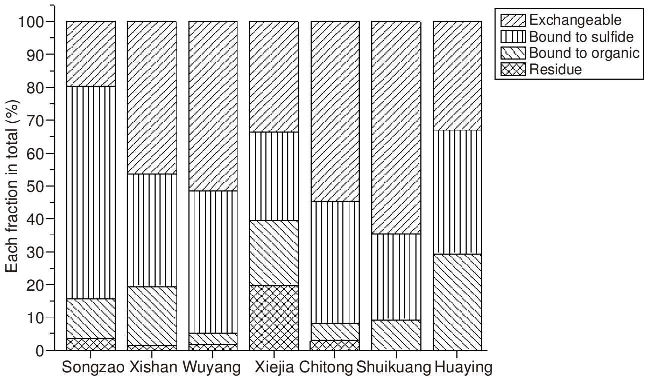

Fig. 2. Pb speciation distributions resulted from the sequential extraction

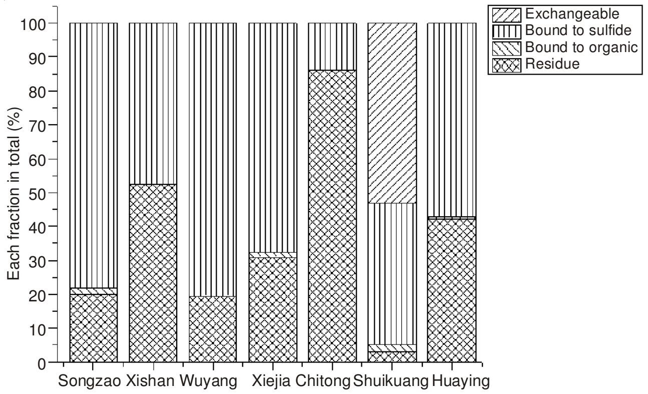

Fig. 3. As speciation distributions resulted from the sequential extraction

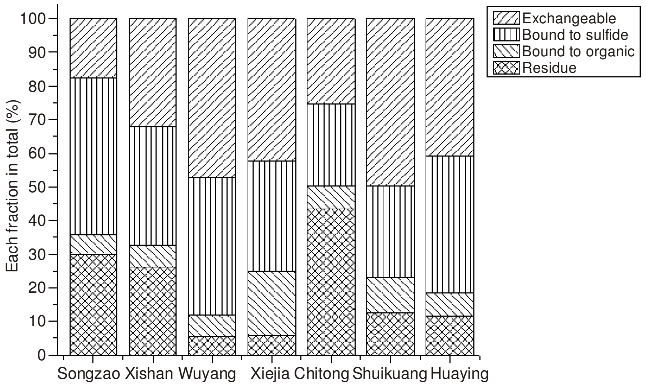

Fig. 4. Zn speciation distributions resulted from the sequential extraction

can also be considered to be a very mobile phase, leaching fraction under some specific conditions. Residue (F4), means the trace elements in this fraction are not expected to be released during a reasonable time because they are usually contained in the crystalline structure of primary or secondary mineral. Lead was mostly associated with galena, clausthalite and other sulfide minerals in coal. The F1 fraction of Pb was in the high percent, especially that in Shuikuang, which was more than half (64.7 %) of the total content. The F2 fraction of Pb ranged from 1.06-8.34 mg/kg and the values of F3 and F4 were low which increase the complexity of migration and transformation of Pb during coal combustion. Arsenic was enriched in pyrite due to its sulfur affinity. F1 fraction of arsenic was below the limit of detection, except that of Shuikuang, the highest distribution of As was in F2, bound to sulfide fraction, ranging from 0.05 to 15.09 mg/kg. The concentrations of As, in F3, were only detected in four of seven samples. Arsenic, in F4 fraction, was stable under certain conditions for its immobility and its fraction were all high in Chitong, Xishan and Huaying. Most of the Zn was distributed in F1 and F2 fractions and the percentage distributions of Zn were inconsistent in different fractions. The distribution trends of Zn, in Xishan and Huaying, were showed in Fig. 3, F2 > F1 > F4 > F3 and that in Wuyang, Xiejia and Shuikuang were F1 > F2 > F3 > F4. Based on the view of chemistry, Zn was symbiotic with sulphide for its sulfur affinity[33].

Statistical linear regression: The A_{ad}, has a sure linear correlation with the content of heavy metal elements in the coal matrix. The state of the target trace element in the coal and its affinity with organic matter can be conjectured and estimated to some extent on the basis of the correlation coefficients[34]. The results of A_{ad} of different coal samples have been displayed in the Table-1, which will be used as X-coordinate data in the process of linear fitting. The content of Zn, Pb and As in the coal are listed in Table-2. Figs. 5-7 have shown the statistical results of linear regression between A_{ad} and Zn, Pb and As content in the coal and the particular fitting equations are listed in the Table-3. It can be easily found that the A_{ad} is proportional to the content of heavy metals from the fitting results of linear regression analysis. The correlation coefficient value is between 0.9 and 1, which means the correlation is very high and the relationship is very close. The correlation coefficient value is between 0.7 and 0.9, which means the correlation is high and the relationship is obvious. When that is less than 0.7, which just means the correlation is medium

TABLE-2
RESULTS OF COAL SAMPLE Aad (%)

Coal samples	1#	2#	3#	4#	5#	6#	7#	8#
A_{ad}	18.80	21.60	3.75	16.95	15.80	21.65	28.75	20.80

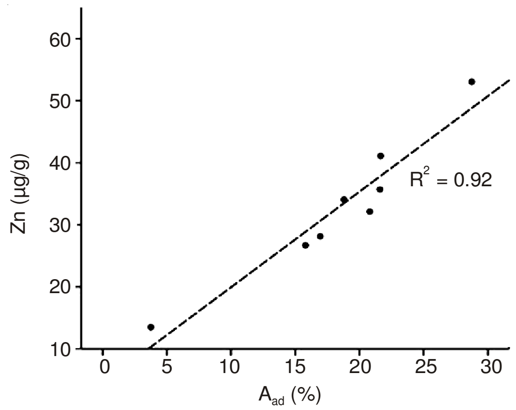

Fig. 5. Statistical linear regression between A_{ad} and Zn content in the coal

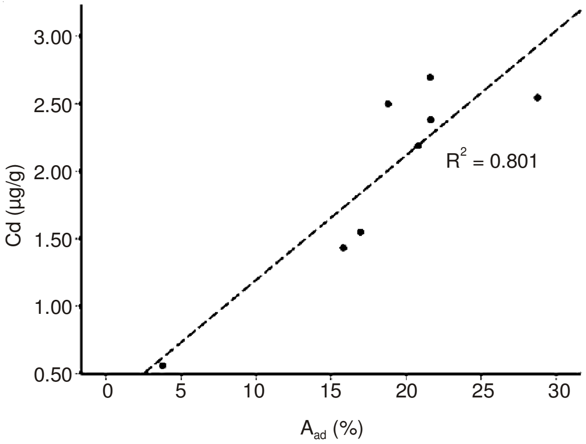

Fig. 6. Statistical linear regression between A_{ad} and Pb content in the coal

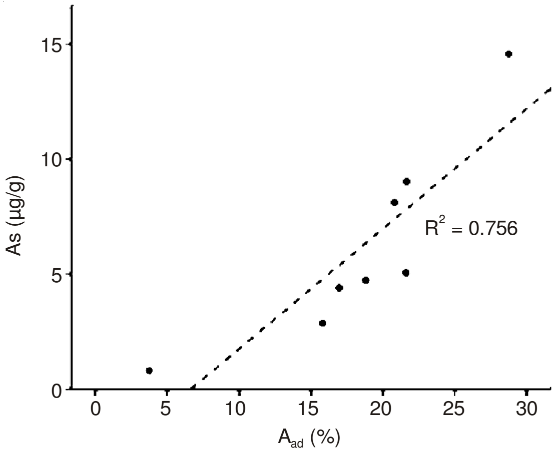

Fig. 7. Statistical linear regression between A_{ad} and As content in the coal

TABLE-3
REGRESSION EQUATION AND CORRELATION BETWEEN ASH AND HEAVY METAL CONTENT

Trace elements	Regression equation	Correlation coefficient
Zn	$Y = 1.540x + 4.530$	0.920
Cd	$Y = 0.092x + 0.272$	0.801
As	$Y = 0.522x - 3.462$	0.756

and the relationship is moderate. Zinc, therefore, the relevance is very high and the correlation of lead and arsenic is obvious which indicates that they are closely related to A_{ad} and exist mainly in the form of inorganic state. The heavy metal elements in coal rarely exist in the form of organic state, just with very little number that is consistent with the results of the speciation distributions resulted from the sequential extraction.

Combustion temperature and λ on the volatilization rate: The combustion temperature and the weight ratio (λ) of the sorbent and coal are two factors that significantly effects the migration process of trace elements and the species formed under the condition of high incineration temperature. Various species have quite different physical and chemical characteristics, which affect the behaviour of heavy metal compounds and capture efficiency. The impact of different combustion temperature and λ on the volatilization rate (%) of Zn, Pb and As in the coal samples have been listed in the Table-4 and sorbent is the calcium carbonate. It is clear that there is a certain relationship between volatilization rate and dosing ratio λ. The volatilization rate of zinc is relatively small, just 56.01 %, when the temperature is 1100 ºC and λ is 1 %. For arsenic, the volatile rate obtained when λ is 1 % is lower than that of 3 % and 5 % at any temperature. The result of the calcium carbonate to reduce the rate of evaporation of cadmium is even more obvious compared with the other two elements and λ of 1 and 5 % are the priority. The increase of dosage of calcium carbonate can cause more ash and slag and reduce the content of fixed carbon. So in order to balance the volatilization rate of the three factors, Zn, Pb and As and the production of the slag, dosing ratio 1 % of the sorbent is accepted for the following experiments when the modified sorbent is used.

TABLE-4
INFLUENCE OF DIFFERENT COMBUSTION TEMPERATURE AND λ ON THE VOLATILIZATION RATE (%) OF Zn, Pb AND As IN THE COAL SAMPLES

Element	Temp. (ºC)		λ = 0	λ = 1	λ = 3	λ = 5
Zn	800	A_{ad} (%)	17.60	19.01	20.87	22.73
		V	54.17	53.49	58.17	52.27
	900	A_{ad} (%)	17.27	17.87	19.73	21.33
		V	66.23	68.53	65.07	53.75
	1000	A_{ad} (%)	20.01	21.07	23.40	23.67
		V	82.50	69.07	59.25	62.92
	1100	A_{ad} (%)	19.20	19.73	21.13	22.20
		V	90.95	56.01	65.32	71.35
Pb	800	A_{ad} (%)	17.60	19.01	20.87	22.73
		V	53.32	48.45	46.23	34.07
	900	A_{ad} (%)	17.27	17.87	19.73	21.33
		V	48.27	37.64	45.38	46.33
	1000	A_{ad} (%)	20.01	21.07	23.40	23.67
		V	73.09	58.06	71.13	46.33
	1100	A_{ad} (%)	19.20	19.73	21.13	22.20
		V	75.49	49.75	60.31	40.90
As	800	A_{ad} (%)	17.60	19.01	20.87	22.73
		V	69.42	62.86	68.22	69.99
	900	A_{ad} (%)	17.27	17.87	19.73	21.33
		V	76.62	72.12	71.44	70.02
	1000	A_{ad} (%)	20.1	21.07	23.40	23.67
		V	82.67	62.89	76.26	65.72
	1100	A_{ad} (%)	19.20	19.73	21.13	22.20
		V	89.15	69.65	80.30	75.49

In order to further investigate the effect of different combustion temperature on volatilization rate of heavy metals by adding calcium carbonate, 0 and 1 % of calcium carbonate were added into the coal at 800, 900, 1000, 1100 ºC combustion temperatures separately and the results are shown in Fig. 8. V1 here means volatilization rate of heavy metals with sorbent and V0 means the rate without any sorbent. From the trend of Fig. 8, it can be seen that the volatile rate of trace elements gradually increase with the rising of the combustion temperature and zinc and arsenic volatilizing rate is close to 90 % at 1100 ºC. The volatilization rate of heavy metals was obviously reduced when $CaCO_4$ was added into the coal sample. Zinc volatilization rates hence have a certain level of reduction from 900 to 1100 ºC and the higher the temperature, the lower the evaporation rate. The volatile rates of lead between 800-1100 ºC were declined, the minimum 37.64 % was obtained at 900 ºC and the addition of calcium carbonate had a negligible impact on the rate and the fixation. Arsenic volatile rates between 800-1100 ºC were also decreased and the optimal value was received at 1000 ºC. On the whole, the addition of calcium carbonate at high combustion temperature have certain control effect on the volatilization of Zn, Pb and As, but the curing efficiency is still low and the capture effect is not obvious.

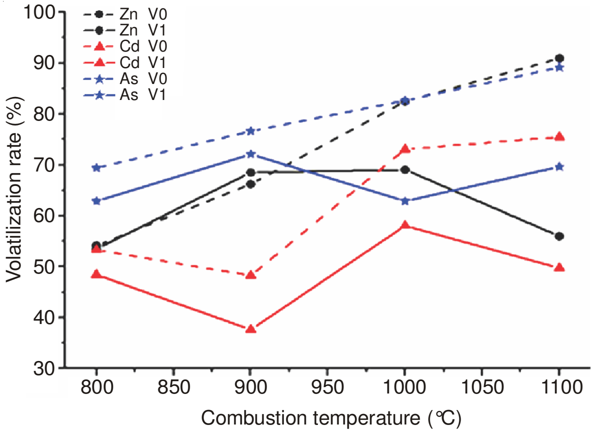

Fig. 8. Effect of combustion temperature on volatilization rate

Capture of the modified Ca-based sorbents for Zn, Pb and As: Calcium ion is the action site of adsorption and chemical reaction with trace elements in the coal in the process of combustion/incineration. The effective contact area between sorbent and coal is one of the most factors that deeply effect the capture efficiency of heavy metals in coal samples. From the above experiment result, it is obvious that the efficiency rate by the addition of calcium carbonate is not very high at high combustion temperature and volatilization rates of zinc, Pb and As are all over 50 %. So it is necessary to modify the traditional Ca-base material to improve its porosity, specific surface area and active sensitivity by taking advantage of some physical and chemical methods. The combustion temperature, additives and γ were selected as controlling factors and every part was divided into three levels. The 1# coal sample was prepared for the experiment and the three levels of the three factors are set as 900, 1000 and 1100 ºC, Na_2CO_3, K_2CO_3 and $Al_2(SO_4)_3$, 10, 15 and 20. Table-5 listed the orthogonal experiment results of Zn, Pb and As.

TABLE-5
ORTHOGONAL EXPERIMENT RESULTS OF Zn, Pb AND As

Number	Temperature (A)	Additive (B)	λ (C)	Volatilization rate (Zn V/%)	Volatilization rate (Pb V/%)	Volatilization rate (As V/%)
1	1 (900 ºC)	1(Na_2CO_3)	1(15)	49.38	29.42	51.8
2	1	2(K_2CO_3)	2(10)	65.50	14.44	43.58
3	1	3($Al_2(SO_4)_3$)	3(20)	61.06	18.63	58.38
4	2 (1000 ºC)	1	2	34.14	46.54	36.05
5	2	2	3	56.28	15.4	39.4
6	2	3	1	18.81	28.22	26.13
7	3 (1100 ºC)	1	3	49.59	36.42	65.77
8	3	2	1	59.06	31.34	67.18
9	3	3	2	51.66	29.47	65.26

It is clear that the capture efficiency of trace elements in coal with addition of MCS is significantly improved compared with the results of calcium carbonate as above. The minimum of volatilization rate for Zn is 18.81 %, which means the 1000 ºC of temperature, $Al_2(SO_4)_3$ of the additive and 15 of γ is the most suitable experimental conditions for the capture of Zn during the coal combustion. In order to examine the significance of factors on the volatilization rate of Zn, the Chi-square value (F) of every part was calculated by using statistical software SPSS Statistics 19. $F_A = 11.988$, $F_B = 4.761$ and $F_C = 1.998$ when the significance level alpha is set as 0.10, which means the power of temperature on the capture of Zn in coal is the most significant, relative to the other factor. The minimum volatilization rate for Pb is 14.44 %, which means the 900 ºC of temperature, K_2CO_3 of the additive and 10 of γ is the most suitable experimental conditions for the capture of Pb during the coal combustion. $F_A = 1.368$, $F_B = 9.031$ and $F_C = 1.372$ when the significance level alpha is set as 0.10, which means the impact of additive on the capture of Pb in coal is the most significant. The minimum of volatilization rate for As is 26.13 %, which means the 1000 ºC of temperature, $Al_2(SO_4)_3$ of the additive and 15 of γ is the most appropriate experimental condition for the capture of As during the coal combustion. $F_A = 9.085$, $F_B = 0.032$ and $F_C = 0.597$ when the significance level alpha is set as 0.10, which means the influence of temperature on the capture of As in coal is the most significant.

Mechanism study of inhibition and capture

Microstructure analysis of modified Ca-based sorbent: From the analytical results of the orthogonal experiment for Zn, Pb and As, it can be easily found that, the different combination of temperature, additive and γ would deeply effect the volatilization rates of trace elements in the coal samples. Although, the impact on the combustion temperature seems significant, the effect of additive and γ will be more important when the temperature is kept constant or at ambient conditions. $Al_2(SO_4)_3$ of additive and 15 of γ is the most appropriate experimental condition for the capture of Zn and As and the effect of $Al_2(SO_4)_3$ on the capture of Pb becomes bigger when the temperature is kept and γ becomes smaller. To examine microcosmic changes in the structure of MCS after the process of modulation, ASAP2010 was used to facilitating the study of different MCS, $Al_2(SO_4)_3$ was selected as additive and γ = 10, 15 and 20 separately were considered. The specific surface area (s) was calculated by BET, the pore volume (v) is calculated by BJH, pore diameter distribution of pore volume or specific surface area was shown in the Fig. 9 and MCS analytical results of microstructure was listed in Table-6.

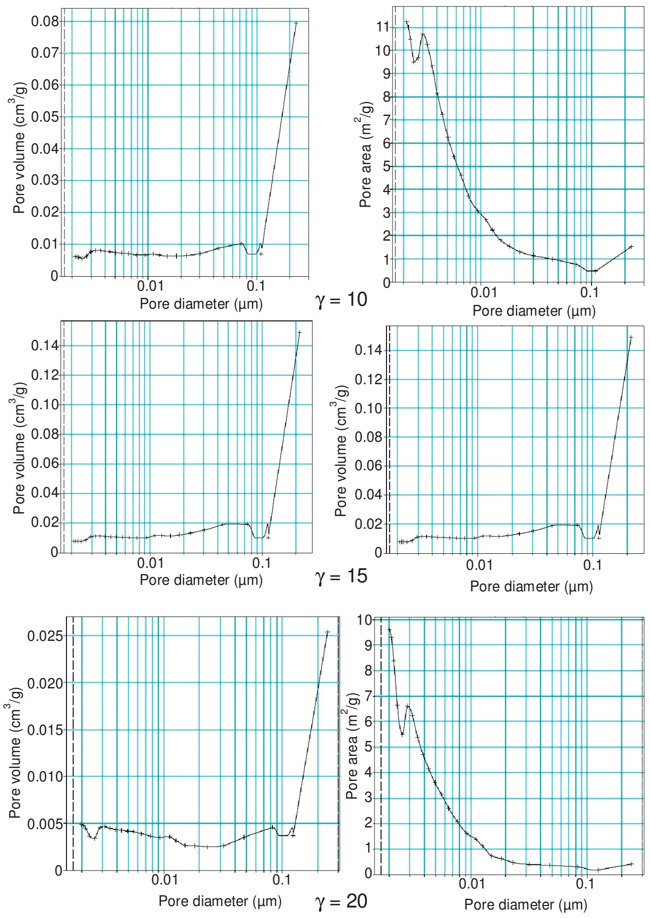

Fig. 9. Pore diameter distribution of pore volume or specific surface area with different γ

TABLE-6
MCS ANALYTICAL RESULTS OF MICROSTRUCTURE

Sample	BET specific surface area ($s/m^2 g^{-1}$)	Pore diameter (d/nm)	Pore volume ($v/m^3 g^{-1}$)
$CaCO_3$	–	< 0.35	–
MCS (λ = 10)	6.1104	10.1316	0.0159
MCS (λ = 15)	9.4433	11.4808	0.0277
MCS (λ = 20)	5.1660	7.2153	0.0087

It is clear that, after the modulation of calcium carbonate, its specific surface area, pore volume and pore diameter are all increased and improved. Possible reasons for this phenomenon are that the ionic radius of the additive metal element is less than calcium ions and they are more inclined to combine with the oxygen in calcium carbonate to form stable chemical bonds. The additive metal ions (Al^{3+}, K^+, Na^+) squeeze into the lattice clearance, replace the position of the calcium ion in the crystal. The replacement form a set number of vacancy and interstitial and cause the defect in the crystal that destroy the original equilibrium state of calcium carbonate crystal, make rearrangement of its internal particles and lattice distortion. The produced defects and cracks increase the contact area between coal and sorbent and reduce the activation energy of ion diffusion, thereby strengthen the capture capacity of heavy metals in the coal during coal combustion.

Surface morphology and energy spectrum analysis (TEM-EDX) of $CaCO_3$ and MCS: SEM-EDX was used to scanning the surface of $CaCO_3$ and MCS [$Al_2(SO_4)_3$, $\gamma = 15$] to intuitively and visually observe the change and difference of surface morphology and microstructure features. Fig. 10 has shown the surface morphology of $CaCO_3$ and MCS magnified by 4000 times and power spectrum diagrams. Calcium carbonate particle is composed of many forms and blocks with sharp edges and the surface of the block body is smooth and compactness. Great changes have taken place in the microstructure of the surface of MCS, the lamellar body surface is rough and porous, with many of the floc and the broken plate shapes, which demonstrate the increase and improvement of specific surface area and internal porosity volume. Al^{3+} of $Al_2(SO_4)_3$ combined with hydroxyl ions generated by hydrolysis in the solution and formed alumina hydrate. The alumina hydrate gradually decomposed under the condition of the heating and γ-Al_2O_3 would accumulate on the surface of the sorbent that would further participate in chemical reactions. Specific reaction equations of γ-Al_2O_3 production as follows,

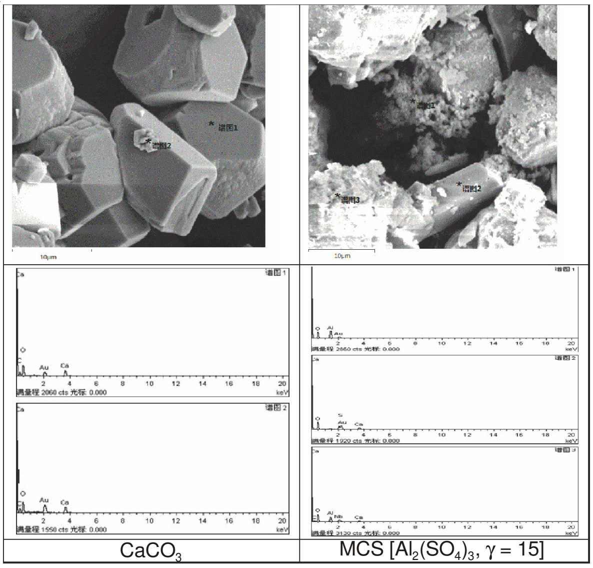

Fig. 10. Surface morphology and energy spectrum scan of $CaCO_3$ and MCS [$Al_2(SO_4)_3$, $\gamma = 15$]

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 \downarrow + 3H^+ \tag{1}$$

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O \tag{2}$$

γ-Al_2O_3 usually called as activated alumina and is produced under the conditions of low temperature (≤ 150 ºC), which is different from the α-Al_2O_3 produced under the condition of coal calcination (950-1200 ºC). The crystal structure of γ-Al_2O_3 is an octahedron or tetrahedral lattice, similar with face-centered cubic and aluminum ions irregularly and randomly distributed in the crystal lattice space. The γ-Al_2O_3 is widely applied as adsorbent and catalyst in industrial applications due to its large porosity, broad internal surface area, high action and strong adsorption. From the result of the power spectrum diagram of MCS, the production of γ-Al_2O_3 on the surface of the sorbent can be easily closed which also describe the influence of $Al_2(SO_4)_3$ on the capture capacity of calcium carbonate.

Melting characteristics of raw coal and coal mixed with MCS: From the trend of TG curves in Fig. 10, the raw coal and the one mixed with MCS ($\lambda = 1$ %, $Al_2(SO_4)_3$, $\gamma = 15$) all have an obvious floating zone, weightless temperature range, 1120-1260 ºC for the raw coal and 1130 and 1250 ºC for the mixed one. Weightlessness is probably caused by the decomposition of carbonate and sulfate mineral in the coal or the heat loss of the hydrate. There will be more apparent peak and valley shown in the curve of DSC, the downward trend means the endothermic property and the upward trend means exothermic property. DSC and TG must be used in combine to examine the melting characteristics of the sample. Pure substance displays just a single peak and a variety of minerals contained at the same will show the overlapping peaks when the reaction process is endothermic and no changes in weight and quality. Tables 7 and 8 listed the characteristic peaks of the DSC curve of the raw and coal mixed with MCS. The raw coal had appeared the overlapping peaks before 900 ºC and showed the features of decomposition and melting. The DSC curve of MCS was relatively flat, does not appear endothermic peak similar with that of the raw coal and the molten phase. At and after 1300 ºC, the curve of MCs was relatively stable and there was still no overlapping peaks which reflected the characteristics of high melting temperature.

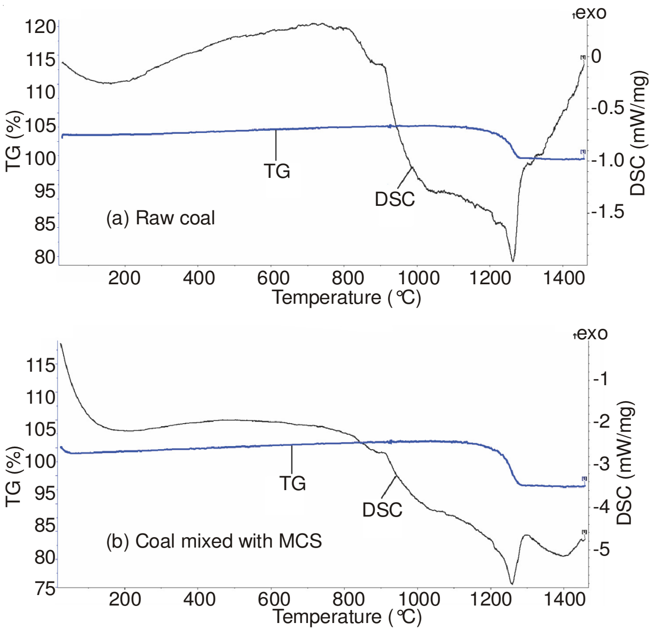

Fig. 11. TG-DSC curves of coal samples

TABLE-7
CHARACTERISTIC PEAKS OF THE DSC CURVE OF RAW COAL

Serial number	Initial temperature (ºC)	Peak temperature (ºC)	Final temperature (ºC)	Remarks
1	741.68	771.55	791.53	Carbonate decomposition
2	861.52	891.67	911.64	Silicate melt
3	1215.98	1267.36	1287.86	Endothermic decomposition
4	1308.44	1329.01	1349.66	Endothermic Melting

TABLE-8
CHARACTERISTIC PEAKS OF THE DSC CURVE OF COAL MIXED WITH MODIFIED Ca-BASED SORBENT

Serial number	Initial temperature (ºC)	Peak temperature (ºC)	Final temperature (ºC)	Remarks
1	1226.23	1267.84	1278.12	Endothermic decomposition
2	1360.53	1401.89	1422.59	Endothermic Melting

Conclusion

The thermodynamic characteristics and mechanisms of migration and transformation of trace elements in coal were discussed based on the study of content, modes of the occurrence, phases, microstructure, morphology and melting properties and the capture of MCS for Zn, Pb, As was studied comparative to the experimental results of calcium carbonate. The content of the same element in the different coal samples was entirely different and the difference of the distribution was very apparent. The content of Zn, Pb and As in most of the coal samples were more than or close to the average and lower than the values of environmental quality standard for soils (GB15618-2008). The main mineral phases of the coal include quartz, kaolinite, pyrite, anatase, silicate, clinochlore and nitrite. Zn and Pb occurred mostly in the form of exchangeable, bound-sulfide and residue in the coal samples and more than 50 % of As was bound-sulfide. Zinc, Pb and As in the most coal samples evaporated and gasified following the priority of As > Zn > Pb during the process of coal static combustion experiment. The relevance of zinc was very high and the correlation of lead and arsenic was obvious which indicated they were closely related to A_{ad} and existed mainly in the form of inorganic state. The addition of calcium carbonate at high combustion temperature have certain control effect on the volatilization of Zn, Pb and As, but the capture efficiency is still low and the result is not obvious. The different combination of temperature, additive and γ would deeply affect the volatilization rates of trace elements in the coal samples, the impact of the combustion temperature was significant and the effect of additive and γ would be more important when the temperature was kept constant. The specific surface area, pore volume and pore diameter of calcium carbonate were all improved after the process of the modulation which effectively increased its capture experience and efficiency. The production of γ-Al_2O_3 on the surface of the sorbent can be easily closed which also describe the influence of $Al_2(SO_4)_3$ on the capture capacity of calcium carbonate. At and after 1300 ºC, there were no overlapping peaks which reflected the characteristics of high melting temperature to modified Ca-based sorbent.

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