C 4.1.4 Co-operative Study on Application of Emission Control Technology for Precursors Causing Acid Rain in the Southwestern China: Analysis of Coal and Control of Fluoride Emission with Bio-briquetting in Chongqing

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Abstract Sulfur dioxide and the other air pollutants emitted from coal combustion were the most important cause of acid rain and air pollution in Chongqing where was suffered from severe air pollution and serious damage. It was known that the fluoride pollution caused health injuries and forests damage. In this paper, the simultaneous control of SO_2 and fluoride emission from coal combustion with bio-briquetting method was investigated. The results obtained from the combustion test of raw coal and bio-briquette indicated that the sulfur and fluoride emissions from bio-briquette combustion were considerably decreased in comparison to raw-coal combustion. Under our experimental condition, sulfur- and fluoride-fixation efficiencies amounted to 90% and 95% respectively. So, bio-briquette containing $Ca(OH)_2$ could be suitable for the control of such pollutants in the district where it had been observed high concentration of fluoride from coal combustion, too. These results suggest that bio-briquetting technology can be applied efficiently to the simultaneous control of SO_2 and fluoride emission from coal combustion in Chongqing.

Key Words: Air pollution control; Bio-briquette; Sulfur-fixation; Fluoride-fixation; Acid rain.

1. Introduction

That air pollution became serious as rapid development of the economy for recent years in China is attended by not only national but also international. It is urgent subject to study control technology for air pollutants. Serious air pollution and acid precipitation in Chongqing was well known[1,2]. Specially, it is afraid that air pollutant emissions from low smoke recourses are harmful to body health[3]. It was well known that not only concentration of air pollutants such as SO_2 and aerosol were very high but also fluoride concentration in atmosphere was high on basis of monitoring data. It is important to use the control measures for fluoride emission in serious pollution regions because gaseous and particle fluoride impacts to body health and forests.

In this paper, the possibility for controlling fluoride emission caused by coal combustion with bio-briquette and its fixation efficiency were discussed, meanwhile the investigation results for fluoride pollution state were reported[4~5].

2. Experimental methods

2.1 Combustion experiment and sampling

In this research, the combustion experiment was conducted in order to investigate fixation efficiency of fluoride with bio-briquetting for coal. Experimental equipment for absorbing gas emitted from raw coal and bio-briquette combustion is shown in **Fig. 1** in order to investigate simultaneous fixation of sulfur dioxide and fluoride.

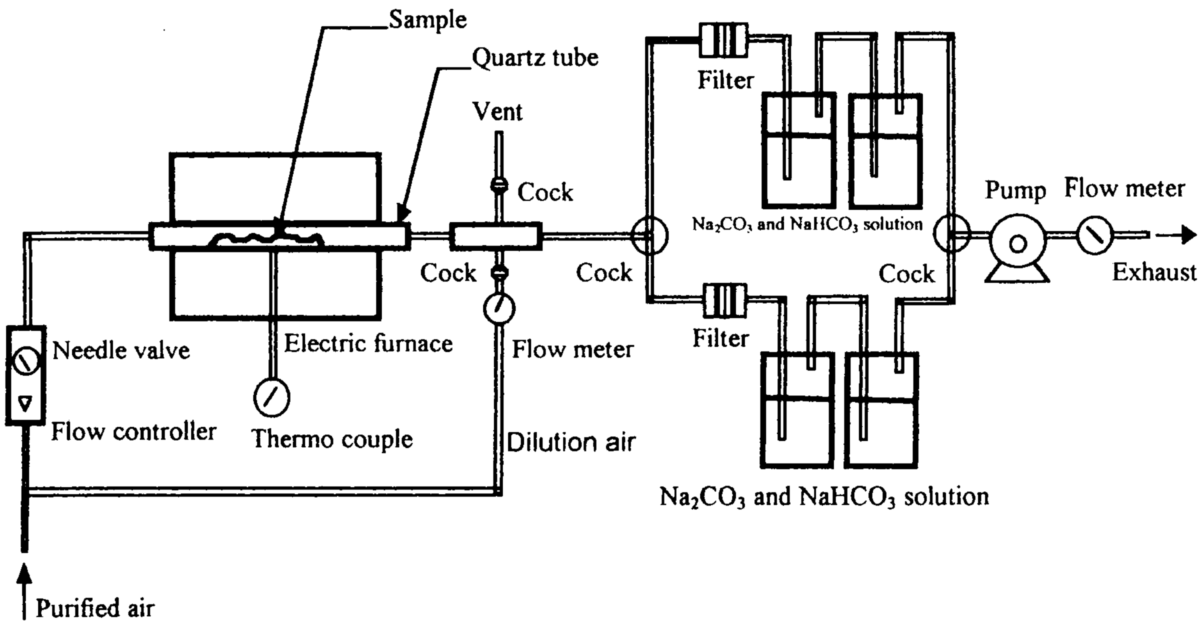

Fig. 1. Experimental equipment for combustion test.

In Fig. 1, 1.000 g of the sample was putted in center of quartz combustion tube. Then, burning gas from flow controller was flowed to electric furnace with the flow rate of 0.5l/min, and the sample was heated by electric furnace from room temperature to 800°C and burned for 10 minutes at 800°C. Temperature in combustion tube was monitored by thermo couple. Exhaust gas from combustion is diluted by 4.5l/min of purified air. The particle was collected on quartz filter (2500QAT-UP, Pallflex Corp.). The exhaust gas was introduced to impinger filled with 150ml of absorption solution (2.7mM Na_2CO_3/0.3mM $NaHCO_3$: eluent solution for anion analysis with an ion chromatograph) in the meantime. Finally, ash remained in combustion tube was measured after it was cooled to room temperature.

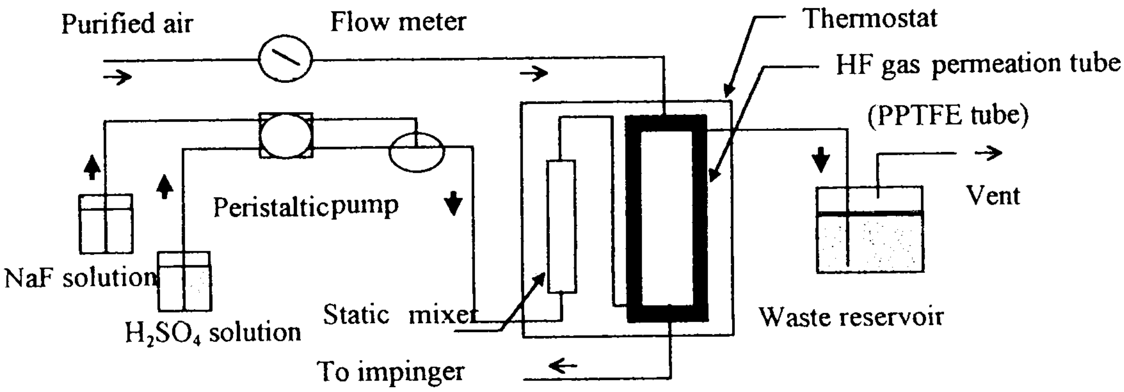

Fig. 2. Schematic diagram of continuous HF gas generating apparatus.

Moreover, impinger and line produced by TEFLON or polyethylene was used in experiment in order to avoid adsorption of fluoride on them. Besides, low concentration HF gas-generating apparatus[6)] shown in **Fig. 2** was used to investigate HF absorption efficiency with 2.7mM Na_2CO_3 /0.3mM $NaHCO_3$ solution. The absorption efficiency of 94% was obtained for 200ppb of fluoride generated in this apparatus.

The particles collected on the quartz filter and residual ash in the combustion tube were extracted with 25ml of distilled water by an ultrasonic cleaning device. Fluoride and sulfate ion concentration in the absorption and extraction solution were measured with an ion chromatograph, and fluoride concentration in gas and particles emitted from coal and bio-briquette combustion was calculated on the basis of these data.

3. Analytical results of coal and sulfur fixation efficiency of bio-briquette

3.1 Analytical results of coal

Elemental concentration of raw coal produced at Tianfu Mines in Chongqing is shown in **Table 1**. Analytical results of raw coal and bio-briquette collected in Tianfu, Nantong and Songzao are shown in **Table 2**[4~5)]. As is clear from these tables, all of Chongqing coals contain a high percentage of the sulfur and ash that may cause air pollution and acid rain. The most of sulfur contained in coal are combustible sulfur and are emitted to atmosphere by combustion. The serious air pollution has occurred in Chongqing due to the complicated terrain and unfavorable meteorological condition for diffusion of air pollutants emitted from combustion of coal with high content of sulfur and ash without treating.

Table 1. Elemental concentration of raw coal produced at Tianfu Mines in Chongqing.

Element	S (%)	Cl (ppm)	F (ppm)
Concentration	3.12	345	107

Table 2. Analytical results of raw coal and bio-briquette in Chongqing.

	Tianfu	Nangtong		Songzao	
	Raw coal	Raw coal	B. B.[a)]	Raw coal	B. B.[a)]
Moisture (%)	1.2	3.1	3.3	1.2	2.0
Ashes (%)	32.5	30.2	30.9	14.4	17.6
Volatilize carbon (%)	16.4	17.0	27.2	14.6	26.0
Fixed carbon (%)	51.1	49.7	38.6	69.8	54.4
Total quantity of heat (kcal/kg)	5570	5600	4890	7180	6190
Total sulfur (%)	3.01	3.30	2.69	2.50	2.05
Uncombustible sulfur (%)	0.16	0.40	2.39	0.21	1.68
Combustible sulfur (%)	2.85	2.90	0.30	2.29	0.37

[a)] Bio-briquettes (B. B.) were produced from 80 wt% of raw bituminous coal and 20 wt% of bagasse by the addition of sulfur-fixation agent (Ca/S=1.5).

3.2 Sulfur fixation efficiency of bio-briquette

The combustion experimental results for raw coal and its bio-briquette of Chongqing and Shenyang were shown in **Table 3**. In Table 3, SO_2-S and SO_4^{2-} -S represent gaseous sulfur dioxide and water-soluble sulfate in particles emitted from coal and bio-briquette combustion, respectively. The ratio of coal and biomass are 3 by weight. Ca/S represents the mole ratio of added $Ca(OH)_2$ to the sulfur content estimated for coal. The sulfur–fixation efficiency calculated from the data of raw coal and its bio-briquette combustion experiment were shown in **Fig. 3**.

Sulfur-fixation efficiency of bio-briquette was calculated by equation (1) on the basis of combustion experimental results for coal, bio-briquette and biomass.

$$E_{SF}(\%)=\{(0.75\times S_0+0.25\times S_B)/(1+\alpha_S\times C\times 74/32-S_{BB}\}/\{(0.75\times S_0+0.25\times S_B)/(1+\alpha_S\times C\times 74/32)\}\times 100 \quad (1)$$

In here, E_{SF} (%), S_0, S_B, α_S, C, S_{BB}, 74, 32 represent the sulfur-fixation efficiency, sulfur emission of coal, sulfur emission of biomass, sulfur content estimated for coal, mole ratio of added $Ca(OH)_2$ to the estimated sulfur content, sulfur emission of bio-briquette, formula weight of $Ca(OH)_2$ and S, respectively.

Table 3. Emission of the air pollutants from combustion of bio-briquette and raw coal (Dry basis).

Sampling sites	Sample	Biomass	Ca/S	SO_2-S (mg/g)	SO_4^{2-}-S in dust (μg/g)	Combustible S (%)	Ashes (%)	Water soluble S of ashes (%)
Datong,	Raw coal			43.33	265	2.18	36.4	0.14
Chongqing	Bio-briquette	Woody dust	1.5[a)]	5.11	10	0.26	29.7	1.13
Briquette plant	Raw coal			30.28	133	1.52	35.8	0.15
in Chongqing	Bio-briquette	Baggase	2.0[a)]	6.24	17	0.15	30.4	0.71
Chongqing	Raw coal			46.47	217	2.33	25.5	0.20
	Bio-briquette	Baggase	2.0[a)]	1.47	7	0.07	22.6	0.47
Jiulongpo,	Raw coal			43.05	139	2.16	38.6	0.16
Chongqing	Bio-briquette	Baggase	2.0[b)]	2.11	15	0.11	30.3	1.12
Jiulongpo,	Refined coal			21.98	24	1.11	16.0	0.08
Chongqing	Bio-briquette	Baggase	2.0[c)]	0.88	3	0.04	12.8	0.78
Shengyang	Raw coal			9.12	20	0.46	14.5	0.27
	Bio-briquette	Rice barn	2.0[d)]	0.93	25	0.05	12.8	0.22

a) The sulfur content in raw coal was assumed 3.0%; b) The sulfur content in raw coal was assumed 3.5%; c) The sulfur content in refined coal was assumed 2.0%; d) The sulfur content in raw coal was assumed 1.0%.

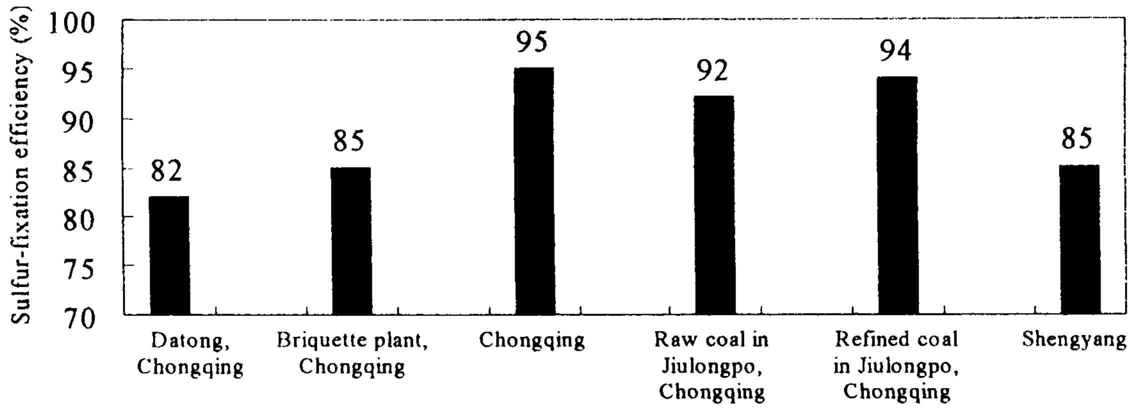

Fig. 3. Sulfur-fixation efficiency calculated based on sulfur emitted from the combustion raw coal and bio-briquette.

As is clear from Fig. 3, it was known that 82~95% of the combustible sulfur was fixed with briquetting of coal and the emission was reduced effectively. Comparing with raw coal, bio-briquette can reduce possibly 90% of SO_2 emission. The results obtained from coal combustion experiment can be summarized in the following.

(1) The sulfur content in raw coal is about 2.5% and the most of them are combustible.

(2) The most of combustible sulfur in coal are emitted in gaseous SO_2. Few particulate sulfurs are emitted.

(3) In comparison with raw coal, the water soluble sulfur content in the ash remained after burning bio-briquette is very low. It is considered that the combustible sulfur was changed to incombustible by the sulfur-fixation reagent added in coal and fixed in the ash.

(4) The ash content in Chongqing coal is high, all of them exceeded 25% and the largest is 38.6% (Chongqing Joulongpo coal). The combustible sulfur and ash of Shenyang coal are low than those of Chongqing, 0.46% and 14.5%, respectively. For this reason, it is considered that atmosphere is polluted by pollutants from the combustion sources of low graded raw coal.

(5) The sulfur content and ash percentage in refine coal is lower than that of raw coal. The cleaning washing of coal can reduce sulfur and ash.

(6) The sulfur-fixation efficiency with bio-briquette added slaked lime is high and amounted to 90% under our experiment condition and the highest value is 95%.

(7) The ash amounts are lower than the value calculated from raw coal, biomass combustion and slaked lime weight. Their abatement rates range 25~37%. The coal energy efficiency is increased.

As is clear from **Table 4**, the combustible sulfur contents of biomass added in the coal are much lower than those of the coal. It is considered that the biomasses contribute little the combustible sulfur of bio-briquette[7].

Table 4. Emission of the pollutants from biomass combustion (Dry basis).

Biomass	Woody dust	Rice bran	Rice straw	Wheat straw	Weeds	Corn stalk	Sorghum stalk	Rice bran[a]	Bagasse
F (ppm)	0	2	4	9	16	21	43	5	--
S (%)	0.006	0.009	0.011	0.019	0.024	0.030	0.039	0.003	<0.1

[a] Rice bran: This sample was collected in Shenyang.

4. Air pollution caused by fluoride in China

4.1 Type of emitted fluoride, emission and effect on environment

Fluoride is a very toxic pollutant, which impacts on human health, animals and plants. Specially, it is able to say that endanger from HF ranks top location in inorganic air pollutants because its toxicity is stronger than other air pollutants such as SO_2.

Major origins of fluoride in atmosphere include metal smelting (specially, Al and Zn), phosphorus acid fertilizer, glass making, ceramics, rocket fuel factory and coal combustion. Specially, high concentration of fluoride in atmosphere occurred timely in the area near metal smelting and phosphorus acid fertilizer factory.

There were various type of fluoride emission, for example, HF, particle fluoride, SiF_4, F_2, organic fluoride. All of these fluoride emissions are main source of air pollution. However, F_2 gas emission is low than others.

Emitted mechanisms for fluoride were summarized as follow.

(1) Burning at high temperature

$$2CaF_2 + SiO_2 \rightarrow SiF_4 + 2CaO \quad (1)$$

$$SiF_4 + H_2O \rightarrow 4HF + SiO_2 \quad (2)$$

(2) Phosphorus acid fertilizer making

$$[Ca_3(PO_4)_2 \cdot CaF_2] + 4H_2SO_4 \rightarrow 2H_3PO_4 + 2HF + 4CaSO_4 \quad (3)$$

4.2 Air pollution caused by fluoride in China

Total fluoride emission amounted to 73.7 thousand tons at ca. 53 cities of China and accounted for 0.17% of total air pollutant emission on the basis of investigation results in 1981. Specially, fluoride pollution was serious in Baotou city of Neimenggu, Lanzhou city of Gansu, Fushun city of Liaoning and Kunming city of Yunnan, and health damage (bone and tooth) caused by fluoride pollution at these areas occurred. Moreover, the effect of fluoride on the generative function of women was reported, too. Fluoride effects mainly absorption for calcium and phosphorus in the human body and destroys internal secret[8-10]. Specially, there was unavoidable destruction on bone and tooth from fluoride. Moreover, the effect of fluoride on the generative function of women was reported as a precedent destroyed internal secret[11]. Beside, concentration of chemical components for fog water, rain water and aerosols was shown in **Table 5**. Concentration in rain water and aerosol in Chongqing and Liouzhou city of Guangxi was high. Fluoride concentration in 182 samples fog collected in Chongqing in 1984-1990 was high, amounted to 1,064 μ eq/l. Fluoride emission caused by metal smelting like zinc at Liouzhou city of Guangxi was amount.

Table 5. Concentration of chemical components for fog water, rain water and aerosols (Unit: fog and rain water, μeq/l; aerosol, neq/m³).

Place	H(m)[a]	Time	Type	n[b]	F^-	Cl^-	NO_3^-	SO_4^{2-}	Σ^-	F^-/SO_4^{2-}	F^-/Σ^-
CS[c]	~200	1984~1990	Fog	182	1064	2062	992	12900	17018	0.08	0.06
RLG[c]	200	1988.3	Rain	42	65	27	52	237	381	0.27	0.17
RLG[c]	200	1988.11	Aerosol	32	61	27	52	584	724	0.10	0.08
ILG[c]	200	1988.11	Aerosol	28	616	111	172	1099	1988	0.56	0.31
SG[c]	400	1988.3	Rain	28	36	14	32	90	172	0.40	0.21
SZG[c]	100	1988.3	Rain	19	32	19	26	32	109	1.00	0.29
MG[c]	2141	1988.3	Rain	28	11	33	55	52	151	0.21	0.07
MG[c]	2141	1988.3	Aerosol	3	11	3	10	88	112	0.13	0.10

[a] H(m): Height above sea level; [b] n: Sample number; [c] CS: Chongqing, Sichuan（四川重慶）; [c] RLG: Residential area, Liuzhou, Guangxi,（広西柳州住民区）; [c] ILG: Industrial area, Liuzhou, Guangxi,（広西柳州工業区）; [c] SG: Shaoguan, Guangdong（広東紹関）; [c] SZG: Sizishan, Guangdong（広東獅子山）; [c] MG: Miaoershan,

4.3 Fluoride content in coal produced in China

The combustion of coal containing high ash is one of major sources of fluoride. The combustion of coal containing tens to hundreds ppm of fluoride emitted amounts of fluoride. And, not only SO_2 and NO_x but also gaseous and particles fluorides were emitted by coal combustion in China which is the largest nation for coal consumption and production in the world[6]. For this reason, it is necessary to understand the behavior for fluoride in atmosphere and its content in coal in order to judge importance of control measure on fluoride in some areas where suffered from serious air pollution.

Fluoride contents in coal produced in various areas of China were shown in **Table 6**[12]. From this Table, it was known that average fluoride concentration (248ppm) of all districts

Table 6. Fluoride content of coal in China (ppm).

Area[a]	SC	YN	GZ	A, SX	WHH	WHB	Beijing	HB	China	World
Sampler number	39	68	3	8	4	16	12	28	328	
Average	554	204	395	1980	1411	466	274	230	248	80

[a] SC: Sichuan（四川）; YN: Yunnan（雲南）; GZ: Guizhou（貴州）; A,SX: Ankang, Shanxi（陜西安康）; WHN: Western Hunan（湖南西部）; WHB: Western Hubei（湖北西部）; Beijing:（北京）HB: Hebei（河北）

was much higher than the average value of world (80ppm), and it produced in some districts amounted to 1,980 or 1411ppm. Moreover, it is estimated that fluoride concentration in the atmosphere is high in Chongqing where the large amounts of coal consumption (16.0 million tons) were consumed although its content in coal is lower than other areas.

5. Possibility of fluoride emission control with bio-briquetting of coal

Up to now, it was known that bio-briquette added biomass and slaked lime in coal can reduce sulfur oxide and dust emission, it was not clear to decrease fluoride emission which is one of the cause for health harmful and forest damage. It is necessary to investigate simultaneous fixation efficiency of sulfur and fluoride emitted from coal combustion with bio-briquette under the best burning condition. Bio-briquette could be used popularly if it posses of ability for controlling effectively fluoride emission. It was thought that fluoride emission is controlled practicably with bio-briquette added slaked lime in some areas where fluoride pollution is serious.

The combustion experiment results and the fixation efficiency of fluoride emission using bio-briquette added slaked lime were shown in **Table 7**. The fixation rate calculated from experimental results and equation (5) was shown in **Fig. 4**. In Table 7, HF-F, F^--F in dust and water soluble F in ashes represents gaseous hydrogen fluoride, water-soluble fluoride in particles and water-soluble F in ashes emitted from coal and bio-briquette

Table 7. Emission of the fluoride from bio-briquette combustion and raw coal (Dry basis).

Sample[a]	DTCQ		BPCQ		CQ		RAJLPCQ		REJLPCQ		SY	
	Coal	B. B.	Coal	B. B.	Coal	B. B.	Coal	B. B.	Coal	B. B.	Coal	B. B.
HF-F (ppm)	91.6	0	84.9	0	51.4	0	88.6	0	21.5	0	30.8	0
F^--F in dust (ppm)	1.6	0.2	14.6	1.2	9.3	0.6	5.2	3.4	1.4	1.2	0.9	0.7
Water soluble F in ashes (ppm)	24.2	84.7	19.8	89.3	22.1	54.5	44.0	86.0	32.9	36.4	60.4	77.3

[a] The names of samples were given in Table 3.

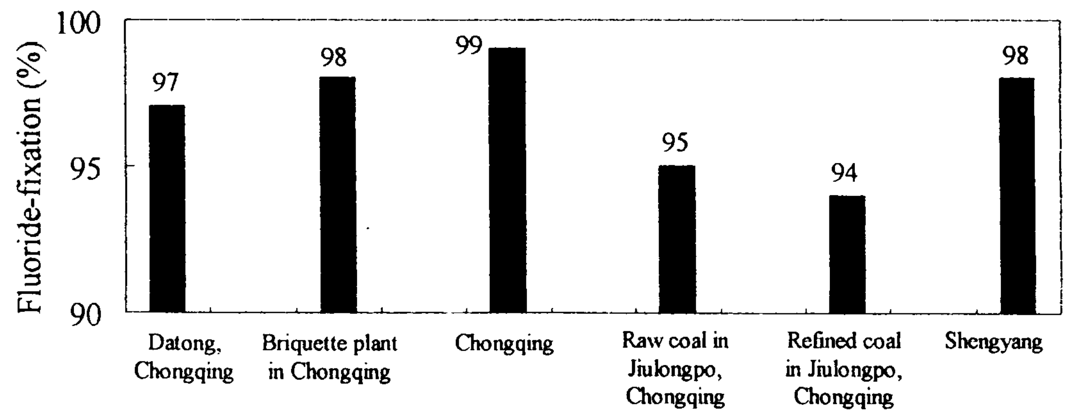

Fig. 4. Fluoride-fixation efficiency calculated based on fluoride emitted from the combustion of raw coal and bio-briquette.

combustion, respectively.

Fluoride contents in raw coal in Chongqing and Shenyang are in the range of 83~138ppm, lower than average level of China, but higher than the average level of world. Specially, the total emission amounts from coal combustion is not low because high coal consumption in that two cities.

In comparison with raw coal, the combustible fluoride through during bio-briquette combustion was transformed to incombustible fluoride and fixed in ashes by the action of added slaked lime, its fixation rate amounted to 94~99%. The emission of gaseous fluoride from bio-briquette combustion was not found, and fluoride concentration in particles was low, too.

It was confirmed that the fixation efficiency of sulfur of raw coal emitted from combustion by bio-briquetting was excellent and simultaneously, the effective emission control of fluoride was good achieved under the optimized combustion condition for sulfur-fixation, too. Therefore, it is expected that bio-briquette contained slaked lime is very useful for the emission control of fluoride in the area suffered from the air pollution caused by sulfur dioxide and fluoride.

6. Conclusion

In this paper, the concentration of fluoride in atmosphere and its contents in coal in China were summarized, and the control of fluoride emission using bio-briquette added slaked lime from coal combustion was investigated with combustion experiment. As the results, it was found that the efficiency of fluoride fixation with bio-briquette was excellent from the combustion experiment for raw coal and bio-briquette. It is thought that bio-briquette added slaked lime is useful because of high ability for simultaneous fixation of sulfur and fluoride. For this reason, bio-briquetties technology is considered to be suitable for some districts suffered from air pollution of sulfur dioxide and fluoride emitted by raw coal combustion.

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