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Emission control for precursors causing acid rain(V): Improvement of acid soil with the bio-briquette combustion ash

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Abstract: The bio-briquette technique which mixes coal, biomass and sulfur fixation agent and bio-briquettes under 3—5 t/cm^2 line pressure has aroused people's attention in view of controlling the air pollution and the acid rain. In this paper, the physicochemical properties of bio-briquette and its ash were investigated. And the acid soil was improved by the bio-briquette combustion ash, which contained nutritive substances such as P, N, K and had the acid-neutralizing capacity(ANC). The pH, *EC*, effective nutrient elements(Ca, Mg, K, P and N), heavy metal elements(Al, Cu, Cd, Cr, Zn and Mn) and acid-neutralizing capacity change of ash-added soils within the range of 0—10%, were also studied. Specially, when 5% bio-briquette combustion ash was added to the tested soil, the content of the effective elements such as Ca, Mg and K rose by 100 times, 7 times and twice, respectively. The total nitrogen also increased by about twice. The results showed the oxyanions such as that of Al, Cu, Cd, Cr, Zn and Mn were not potentially dangerous, because they were about the same as the averages of them in Chinese soil. It is shown that the ANC became stronger, though the ANC hardly increases in the ash-added soil. On the basis of the evaluation indices, it is concluded that the best mixture ratio is to add 2.5%—8% of the bio-briquette combustion ash to the tested soil.

Keywords: bio-briquette combustion ash; soil improvement; ANC; heavy metal element; nutrient element

Introduction

In China the land deserted for natural or artificial reasons already exceed 27% of the total land area and it continues increasing by an average rate of 2400 km^2/a. Furthermore, the energy consumption has been increasing with Chinese economic high-speed development. Supply of and demand for coal also increase rapidly, and it is expected to reach about 1.5 billion t/a in 2000(Yan, 1997). The discharged SO_2 and dust from coal combustion have increased rapidly. Environmental acidification and the increase of SO_2 discharge, which are closely related each other, will lead to the expansion of an acid rain area and the acidification of soil (Wang, 1996). Especially, acid rain due to serious air pollution has been observed in southern China since 1980's. Recently, acidification of precipitation has been experienced, and the frequency of acid rain also becomes higher, it appears even at Qingdao and Tuman in northern China. Therefore, the soil acidification becomes increasingly severe in acid rain area.

The often-used measure dealing with environmental acidification is to spray some substances such as calciclase ($CaCO_3$), dolomite($CaMg(CO_3)_2$) and so on, to the rivers, lakes and forests. This method has been widely used in northern Europe(Abrahamsen, 1996). It became a national policy in 1977. It has been carried out until now in Sweden. It is also standardized in China, and improvement of the cropland acid soil with the lime materials is normally used as the soil improvement method. When soil is acidified, exchange base is often insufficient in the soil, the lime materials are employed to raise soil pH to its appropriate acidity. So it is considered to be one of the easiest methods to correct the acidified soil.

At present, the bio-briquette technique is one of the most effective methods to control the air pollution, and it has aroused people's attention for its high sulfur fixation(70%—90%; Wang, 1999). Not only can the bio-briquette technique be used to control air pollution, but also the nutrient elements such as P, N, K and the acid-neutralizing capacity in the bio-briquette combustion ash can be supplied to the acid soil to improve it. It is expected to! present zero emission recycle when the bio-briquette combustion ash as waste product is used to improve acidic soil. Therefore, the chemical characteristics of the coals, the biomass, the bio-briquette and its combustion ash are investigated, the nutrient elements and heavy metal elements in the bio-briquette combustion ash supplied to acid soil are measured in our study. The chemical analysis of ash-added soil is carried out, and the improvement effect of pH, *EC*, effective elements (Ca, Mg, K, P and N) and the acid-neutralizing capacity in ash-added soils are studied. The best mixture ratio of bio-briquette combustion ash added to the tested soil is also discussed.

1 Experimental methods

1.1 Preparation of the tested soil and the bio-briquette

combustion ash

The acidic soil (yellow earth) used in this study was collected in Chongqing, a typical acid rain area, in December 1998. The sampling point named Longjingcun is about 20 km away from central Chongqing. The bio-briquette is made from Songzao coal (produced in Chongqing; 75%), biomass (wheat straw; 25%) and sulfur fixation agent $Ca(OH)_2$ (Ca/S (mole/mole) = 2) under 3—5 t/cm^2 line pressure. The bio-briquettes were burn in an electric furnace according to JIS M8812 and the ash is collected. Furthermore, the improved soils are made of the tested soil and the ash with 7 different weight ratios ranging from 0 wt% to 10 wt%.

1.2 Elemental analysis of the tested soil and the combustion ash of bio-briquette

2 g of the tested soil or the ash sample is placed in 50 ml Teflon cups and treated it with $HF\text{-}HNO_3\text{-}HClO_4$ according to the procedures in Fig.1 (Sun, 1990). The treated soil or the ash is dissolved and diluted with 5% HNO_3. The solutions are analyzed for main elements and trace elements such as Ba, Ca, Cu, Cr, K, Mg, Sr, Zn, Mn, Al, Fe, Na and Ni using inductively coupled argon plasma emission spectroscopy (ICP). Furthermore, the analysis conditions of ICP are given in Table 1 and Table 2.

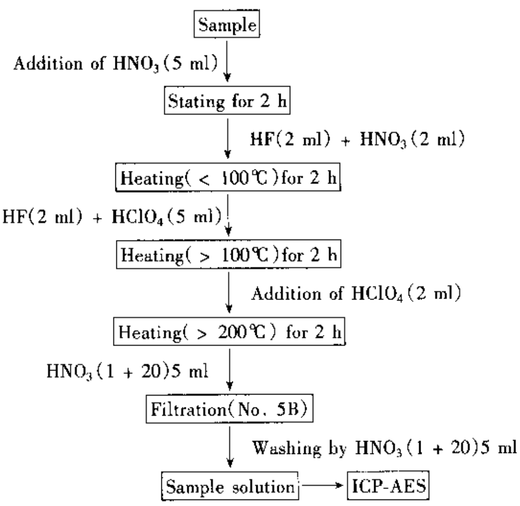

Fig.1 Experimental procedure of acid extraction

Table 1 Instrumentation and operating conditions

Item	Condition
Instrumentation	JICP-1000 UV
Nebulizer	38 P/in^2
Pumping rate of sample	1.2 ml/min
Power	1.0 kW
Frequency	27.12 MHz
Argon flow	
Coolant	13 L/min
Auxiliary	1.0 L/min
Analytical condition	
Number of integration	3 times
Uptake time	20 s
Scanning integration time	5 s

Table 2 Analyzed elements and its detection wavelength

Elements	Wavelength, nm	Elements	Wavelength, nm
Ca	396.847	Cu	324.754
Al	308.215	Zn	213.856
Fe	259.940	Ni	231.604
Mg	279.553	Sr	407.771
K	766.490	Cd	214.438
Na	589.592	Mn	257.610
Cr	267.720		

1.3 Measurement of N and P in tested soil and combustion ash of bio-briquette

20 mg of sample which was passed through a 2 mm sieve is placed in a quartz boat, for total nitrogen measurement with NC Analyzer (Sumitomo Chemistry Company, NC-80).

2 g of dry sample which was passed through a 2 mm sieve entered a 1 L of triangular flask or oscillation bottle, and treated with 400 ml extracting solution for 30 min. Then the treated sample is filtered with the 0.45 μm filter (No. 5B). 20 ml solution from upper of the base solutions is added with 2 ml of K_2SO_4 solution. It is dissolved for 1 h at 110℃ in the autoclave. The total phosphorus in cooled solutions is measured by a spectrometer (Shimadzu Co., UV-1200).

1.4 pH, *EC* and water-soluble ions of the ash-added soils

The pH of the soil is measured using electrode method as reported in the previous paper (Dong, 1999). And, a sample of 5.0 g is mixed with 25 ml of ion exchange water (1 :5 w/w), and shaken (oscillation speed: 100 ± 10 times/min) at 25℃ for 30 min. After lying up for 30 min, the *EC* of the solutions are measured by *EC* meters (Model-CM78, TOA Co.). Remaining solution is filtered with 0.45 μm of filter (No.5B), and the ion concentrations in the filtrated solution are determined by ICP under the experimental conditions as described in 1.1.

1.5 Measurement of acid-neutralizing capacity in soil

The H^+ amount consumed by whole exchange base and mineral in the soil is defined by V. Breemen as acid-neutralizing capacity. The acid-neutralizing capacity (ANC) is the sum of carbonate and exchange base capacity ((ANC) c), and sulfuric acid of adsorption amount ((ANC) a) by soil.

1.5.1 Carbonate and exchange base capacity ((ANC)c)

1 g of dry soil sample (D < 2 mm) was added to 50 ml of 0.5 mol/L $CH_3COOH\text{-}CH_3COONH_4$ buffer solutions (pH 4.7), and is shaken to extract at 25℃ for 24 h. Then the soil sample is separated from the base solution by centrifugation and decanting. The upper solution is filtrated by 0.45 μm filter with suck pump. The Ca^{2+}, Mg^{2+}, Na^+ and K^+ concentrations in the filtrated solution are measured by an atomic absorption spectrophotometer. The sum of Ca^{2+}, Mg^{2+}, Na^+ and K^+ concentrations in the filtrated solution is defined as C1. The concentrations of water-soluble Ca^{2+}, Mg^{2+}, Na^+ and K^+ are determined using ion

exchange water instead of the buffer solution. The sum of their concentrations is defined as C2. The difference between C1 and C2 converted into milliequivalent per 100 g soil is defined as(ANC)c.

1.5.2 Amount of sulfuric acid absorbed by soil((ANC) a)(acid-neutralizing capacity based on soil adherence of SO_4^{2-} in the precipitation)

1 g of dry soil sample(D < 2 mm) was added to 50 ml of 1.56×10^{-3} mol/L K_2SO_4 solutions(as S is 50 mg/L). After the pH of the solution becomes 4.7 with 1.0 mol/L HCl, it is shaken and extracted at the room temperature for 24 h. Then the soil sample is separated from the base solution by centrifugation and decanting. The upper solution is filtered by 0.45 μm filter. The SO_4^{2-} concentration difference between the former and latter experiment converted to milliequivalent per 100 g soil is defined as(ANC)a.

2 Results and discussion

2.1 Composition of raw coal and biomass, and sulfur-fixation rate of bio-briquette

The basic analysis results of Songzao coal and wheat straw are shown in Tables 3 ane 4. As is clear from the tables, the coal contained a high percentage of the sulfur and ash, and reached to 2.73% and 29.2%, respectively. The most of sulfur contained in coal is combustible sulfur, which is emitted to atmosphere during combustion. From Table 4, we found that the sulfur-fixation efficiency with bio-briquette added $Ca(OH)_2$ was very high and amounted to about 84% under our experiment conditions, and fixation efficiencies of HCl and dust were 65% and 61%, respectively. The sulfur fixation agents used most frequently are the calcium-based materials such as $Ca(OH)_2$, $CaCO_3$ and CaO. We used the $Ca(OH)_2$ in this study, because of its excellent sulfur-fixation efficiency. After combustion, a certain amount of calcium-based materials will be remained in bio-briquette ash. Therefore, we try to improve acidic soil with the ash remained after burning the bio-briquette in this study.

Table 3 The basic analysis of coal and biomass used in producing bio-briquette(dry basis)

Sample	Sulfur, %			Ash,	Volatile matter,	Fixed carbon,
	Combustible	Incombustible	Total		%	
Songzao coal	2.47	0.26	2.73	29.8	12.7	55.1
Wheat straw	0.02	/	/	8.2	80.1	10.4

Table 4 Emission of the air pollutants from Songzao coal and its bio-briquette combustion, and reduction efficiency of pollutants by bio-briquetting(dry basis)

Sample	Emission, mg/g-coal			Combustible S, %	Reduction efficiency, %		
	HCl	SO_2	Dust		Dust	HCl	SO_2
Songzao coal	0.39	49.49	2.25	2.47			
B.B*	0.11	5.48	0.79	0.27	65	61	84

Notes: * Bio-briquettes(B. B.) were produced from 75 wt% of Songzao coal and 25 wt% of wheat straw by the addition of sulfur-fixation agent($Ca(OH)_2$)(Ca/S = 2.0)

Table 5 The contents of elements of yellow earth collected in Chongqing

Elements	Ca	Mg	K	Na	Al	Fe
	mg/g					
Top-soil	0.34	2.79	10.51	0.71	53.60	32.77
Bottom-soil	0.35	3.04	11.75	0.71	51.42	24.90

Elements	Cu	Mn	Cr	Zn	Ni	Cd
	μg/g					
Top-soil	155.6	101.7	73.0	41.8	16.7	0.1
Bottom-soil	155.0	117.4	73.1	55.1	18.4	0.1

2.2 Analytical results of the tested soil and discussion

The main factors that hamper crop growth in the acid soil are as follows: (1) low pH value; (2) surplus of Al; (3) inadequate alkaline metals (K, Mg, Ca); (4) inadequate P; (5) trace metal elements; (6) weak microbe activity(Saegusa, 1991). In order to improve such harmful soil, it is necessary to understand the physicochemical properties of the soil. Therefore, their contents of various elements according to the tested soil (yellow earth in Chongqing) were determined layer by layer and are shown in Table 5. The samples of the top layer soil(top-soil) and the bottom layer soil(bottom-soil) were collected from 0—5 cm and 5—20 cm of depth under the ground surface, respectively.

Table 5 shows clearly that the basic elements' contents (Ca, Mg, K and Na) were much lower than the average value of the Chinese soils, and Al, Fe and Mn contents were a little higher. It is considered that their contents are depended on the geographic feature and atmospheric conditions of Chongqing. Chongqing belongs to the subtropical zone with high humidity, high temperature climate and about 1000 mm precipitation annually. So the plants and crops grow rapidly in this area, and accumulation of organic matter and the microbe activity are very high. At the same time, the decaying speed of rock is fast, and the basic substance becomes poor in weak acidic soil. Especially when the acidity of the precipitation is as high as pH 4.07—4.52. Also, the acid rain region has become wider, and the frequency of acid rain has reached 70% or more. The soil was deficient in basic substance very much, because Ca and Mg in the soil are washed out continuously. As the result of washing out, Table 5 shows that the contents of basic elements in the bottom layer soil were higher than that in the top layer soil. On the other hand, Al and Fe contents were much higher in the top layer soil. This is the reason why the extreme geochemistry process named aluminum accumulation process (Dong, 1999). While silicate in soil was resolved rapidly, the silicon and basic substance were washed out, so that the oxides of Fe and Al were accumulated obviously in the surface soil, and they became the second minerals and granular clay slowly in this process (Dong, 1991).

The physical and chemical characteristics of the tested soil are shown in Table 6. Table 6 shows that the pH of the soil is only 4.19, and the *EC* is very low. It presents the typical acidic soil. On the other hand, aluminum ion concentration demonstrates high level. It will lead to the damage of plants. The acidity of soil is one of an important feature of the yellow earth. When its acidity becomes lower, the Al^{3+} concentration tends to be higher. The base saturation degree is only 20%, because the yellow earth in Chongqing is exposed to the acidic atmosphere and the acid rain for a long time. Table 6 shows that the water-soluble ion concentrations in top layer soil are higher than that in bottom soil obviously. It is assumed that both the temperature and the humidity in this area were high, and organic matter and the humus in the top layer soil were high, so the substance circulation and microbe activity were active and a lot of elements existed in ion states. When pH of the yellow earth condition is below 4.5, normal plants and crops can not grow up except tea trees and the high acid plant such as rubber trees. In order to extensively remove Al^{3+} ion which is strongly toxic to the plants and crops, it is necessary to spray the basic substance to agriculture and forest areas that are serious acid rain areas.

Table 6 pH, *EC* and water-soluble ions of yellow earth collected in Chongqing

Elements	pH* (H_2O)	*EC*, dm/s	Ca^{2+}	Mg^{2+}	K^+	Na^+	Al^{3+}	Fe^{3+}	Cu^{2+}	Mn^{2+}	N	P
			meq/L								mg/g	
Top-soil	4.19	65.2	151.5	37.5	52.0	0.9	77.6	9.1	2.2	4.0	1.9	4.08
Bottom-soil	4.29	63.1	133.0	32.6	54.3	0.9	63.3	5.2	0.4	2.6	1.8	2.94

Notes: The soil was extracted with ion exchange water (1:5) for 1 h; * the soil was extracted with ion exchange water (1:2.5) for 1 h

2.3 Chemical properties of the biomass and the bio-briquette combustion ash

In order to improve acid soil with the bio-briquette combustion ash, it is very important to understand the chemical properties, chemical components and elemental contents of wheat straw and the bio-briquette. Their elemental analysis results are given in Table 7. Table 7 showed that the contents of nutrient elements in wheat straw used in our study were high, especially Mg, K, N and P content were very high, and reached 7.62 mg/g, 22.2 mg/g, 7.8 mg/g and 6.2 mg/g, respectively. However, the toxic heavy metal contents such as Cu, Cd, Cr, Zn and Mn were not high in the wheat straw. Therefore, it is considered that the effective nutrient elements are supplied when the acidic soil is mixed with adequate amount of the ash.

From Table 7, we also found that the basic elements contents in the ash were high, especially for Ca content. It was found that the ash not only has high buffering ability to the acidic substances, but also solves the problems such as the shortage of basic substances in acidic soil. It is clear that the N and P contents in the ash were very high and reached 5.9 mg/g and 5.47 mg/g, respectively. We may reasonably concluded that the toxic heavy metals, such as Cu, Cd, Cr, Zn and Mn, do not polluted soil because their contents were the same level as the average contents of those elements in Chinese soil, or within the normal ranges of them. So when the acidic soil is improved by the ash, it is expected that the basic saturation degree becomes high, the acidity becomes low, trace nutrient elements are supplied to plants and crops, but not lead to plants and crops to be damaged with the heavy metal elements in improvement soil. Therefore, it is deduced that the ash is possible enough as an additive of acid soil improvement.

Table 7 Content of metal elements in biomass and bio-briquettes combustion ash

Elements	B.B* ash	Wheat straw ash	Chinese soil average value (range)
Al, mg/g	22.2	6.18	66(34—98)
Fe, mg/g	19.5	3.20	29(10—48)
Ca, mg/g	90.0	1.75	15(0.1—48)
Mg, mg/g	4.5	7.62	8(0.2—16)
K, mg/g	4.9	22.1	19(9—28)
Na, mg/g	2.3	9.3	10(0.1—23)
Sr, μg/g	643.4	110.3	167(21—690)
Mn, μg/g	672.1	363.6	583(130—1786)
Cu, μg/g	406.7	112.0	23(7—272)
Zn, μg/g	126.8	95.3	74(28—161)
Cd, μg/g	0.4	0.1	0.1(0.02—0.3)
Cr, μg/g	50.0	29.1	61(19—150)
Ni, μg/g	69.5	52.5	27(8—71)
Ba, μg/g	183.2	87.1	467(251—809)
N, mg/g	5.9	7.8	/
P, mg/g	5.4	6.2	/

Note: * Refer to Table 4

2.4 Acidic soil improvement

2.4.1 Changes in pH and *EC* of the soil added with the bio-briquette combustion ash

pH and *EC* of the soil are main indexes to evaluate the quality of agriculture soil. pH is a synthetic index that reflects the acidification level of soil, and *EC* is also as an index that reflects the water-soluble base amount in soil. They are widely used in soil study. Therefore, it is very important to consider pH and *EC* in ash-added soil when we improve the acid soil with the addition of the bio-briquette combustion ash.

pH and *EC* change of ash-added soils, which were divided into 7 categories within the range of additive ratio 0 wt%—10 wt%, are shown in Fig. 2 and 3. pH of the top and bottom layer soils added with 2 wt% of the ash became 5.6 and 5.8 or more, respectively. pH of soils can be classified in the range of 5.0—6.5, 6.5—7.5 and 7.5—8.5, which correspond to the weak acidic soil, the neutral soil and the weak alkaline soil, respectively. Fig. 2 shows that pH of the top layer soil became 5.6—8.5 when the tested soil was added with the ash of 2 wt%—8 wt%. It is considered that the plants and crops grow up well in soil added with the ash within the range of pH 6.5—8.5(neutral-weak alkaline soil) in the areas where serious air pollution and acid rain occur frequently. Fig.3 shows that *EC* of the ash-added soil increased gradually with the rise of mixing ratio in the ash until the ratio reached 2.5 wt%. When it became 2.5 wt% or more, the increasing tendency of *EC* became almost flat. Because the electric conductance is an index of the ion activity in solution, the ion activity is increased in the soil solution added with the ash, so growth and harvest amount of many crops are expected to rise. It is reported that the crop harvest reduces when *EC* of the soil solutions exceeds 4000 ds/m. There is no need to worry about damaging in plants and crops by increasing *EC* in the ash-added soil, because the change in *EC* of soil added with the ash of 2.0 wt%—10 wt% was only about 1100—1600 ds/m in our study. Furthermore, from Fig. 2 and 3, it is considered that the most suitable mixing ratio to improve acid soil with the ash is in the range of 2.5%—8.0 % in this study.

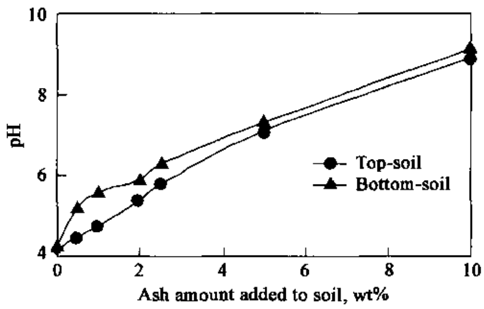

Fig.2 Effect of ash-addition on pH of soil

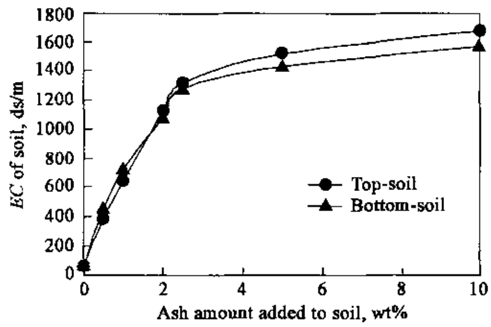

Fig.3 Effect of ash-addition on *EC* of soil

2.4.2 Changes of metal elements in soil added with the bio-briquette combustion ash

Under the normal soil environment, the main cations are Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} and Al^{3+}, and they are adhered as hydrate ions with electrostatic charge. Since soils have been washed by low pH acid rain for a long time in Chongqing, the basic cations such as Ca^{2+}, Mg^{2+} and K^{+} are washed out to underground water due to the ion exchange reaction, and the basic substances of the top layer soil are very poor. In order to restore the nutrient elements, the tested soil was added with the bio-briquette combustion ash, which contained extensive basic substances. The changes of the basic elements and the nutrient substances in the soil added with the ash within the range of 0 wt%—10 wt% are shown in Table 8.

Table 8 shows that the increase in nutrient concentration is obvious in the ash-added soils. When 5% of the ash was added to the acid soil, the water-soluble Ca^{2+}, Mg^{2+} and

Table 8 Total N, P and water-soluble ions in yellow earth added with bio-briquette ash

Soil	Ash amount added in soil,	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	N	P
	%	meq/L				mg/g	
Top soil	0	151.1	37.5	52.0	0.9	2.9	4.08
	0.5	2599.5	145.0	60.0	12.6	3.8	4.09
	1.0	5725.0	210.0	62.1	20.9	4.0	4.14
	2.0	12295.0	269.2	63.3	25.6	4.0	4.04
	2.5	13525.0	285.0	76.2	40.0	4.1	4.14
	5.0	16000.0	318.3	90.8	73.5	4.7	4.20
	10.0	17712.0	335.1	112.8	157.4	5.8	4.42
Bottom soil	0	133.0	32.6	24.3	0.9	1.8	2.94
	0.5	3692.0	122.5	25.0	8.3	2.2	nd*
	1.0	7145.0	175.0	26.7	17.7	2.4	nd
	2.0	11550.0	185.8	24.5	18.4	2.5	nd
	2.5	12555.0	190.7	26.7	20.9	2.9	nd
	5.0	14125.0	216.7	37.1	23.9	3.2	nd
	10.0	16832.0	293.1	61.5	77.4	4.1	nd

Notes: Soil was extracted with ion exchange water(1:5) for 1 h; * nd: not determined

K^+ concentrations both in the top and bottom layer soils were about 100 times, 7 times and 2 times more than that in the tested soil, respectively. And in the 10% ash-added soil, one of the most important elements, total nitrogen reached twice higher than that of the tested soil. The total basic cation in the top layer soil added with 5% of the ash became 16.5 meq/L from 0.25 meq/L in the tested soil. Moreover, the acidic tested soil (pH 4.19) also became neutrality soil (pH 7.53) with the addition of the ash.

The increase in the indexes with each restoration in the top layer soil was higher than that in the bottom soil. Therefore, the restoration effect on the top layer soil was obvious with large amounts of humus acid in the top layer soil and active microbe, the ash added to the soil is reacted rapidly with them.

On the other hand, the changes in ion concentrations of trace elements in the improvement soil are shown in Table 9. It was found that the increasing tendency of ion concentrations was positively related to the rise of the additional amount. On the contrary, the concentrations of Al^{3+}, Fe^{3+} and Ni^{2+} became lower oppositely though the changes were very small. The reason is that the acidity became lower, pH became higher, and the solubility of Al^{3+}, Fe^{3+} and Ni^{2+} reduced in the solution of improvement soil added with the ash. At the same time, a greater availability of P, as a result of mycorrhizal infection provided a high degree of resistance in plants against the toxicity of metals so that their accumulation in foliage was greatly reduced (Rahman, 1996). In Table 7, the concentrations of Cu^{2+}, Cr^{3+} and Cd^{2+} are increased substantially, when additional amount of the ash exceeds 10%. We believe that the addition of 10% or less of the ash is suitable to improve acidic soil in Chongqing in this study.

Table 9 Trace metal elements water-soluble ions in yellow earth added with bio-briquette ash

Soil	Ash amount added in soil, %	Al^{3+}	Mn^{2+}	Cu^{2+}	Sr^{2+}	Cr^{2+}	Fe^{3+}	Zn^{2+}	Ni^{2+}	Cd^{2+}
		meq/L								
Top soil	0	63.3	4.0	2.20	10.7	0.3	9.1	1.2	0.15	0.06
	0.5	56.8	6.55	2.52	11.9	2.1	10.2	1.8	0.13	0.05
	1.0	67.6	6.55	2.27	19.9	5.2	15.3	1.0	0.15	0.05
	2.0	56.2	4.36	2.51	43.8	8.7	16.2	0.9	0.06	0.03
	2.5	50.7	6.55	2.58	64.4	8.2	19.8	1.8	0.03	0.04
	5.0	51.6	5.1	2.52	77.6	8.7	17.6	1.0	0.06	0.07
	10.0	45.5	6.8	12.6	95.0	12.4	23.6	1.9	0.09	0.12
	20.0	47.7	7.1	15.6	134.9	19.2	5.9	2.6	0.17	0.21
	40.0	45.5	14.2	25.0	158.3	25.5	4.3	4.2	2.1	0.21

2.4.3 Acid-neutralizing capacity (ANC) of the ash-added soil

The reduction of ANC of soil is similar to acidification of the soil. If ANC is used up, the toxic Al^{3+} is dissolved from soil to the plants. Therefore, it is very important to understand the change of the ANC when we examine the improvement effect of acidic soil with addition of the bio-briquette combustion ash.

The change of ANC in the ash-added soil is shown in Fig.4. The ANC is the sum of carbonate, exchangeable base capacity ((ANC)c) and adsorption amount of sulfuric acid ((ANC)a) by soil. Fig.4 shows that ANC of the top and bottom layers in tested soil were about 7.3 meq/100 g and 7.8 meq/100 g, respectively. The ANC values correspond to the low ANC and this classification is based on Sato's report (Sato, 1993). It is clear that ANC of Chinese soils are correlated with geographic feature. For example, all ANCs are 5 meq/100 g or less in southern China (especially in Fujian Province); while all ANCs are almost 12 meq/100 g or more in northern or northwestern China. It is considered that their values are related to the kinds of soils, the weather condition and frequency of acid rain in those areas. Fig.4 also shows that the acid-neutralizing capacity in the top and bottom layers of tested soil increased jointly with the rise in the mixing ratio of the combustion ash. The ANC of the top layer soil added with the bio-briquette combustion ash is bigger than that of the bottom's, it reached 82 meq/100 g. Fig.4 shows that (ANC)c increased with the rise in the mixing ratio of the combustion ash addition, while (ANC)a of the improved top and bottom layer soils hardly increased. It is assumed that (ANC)a has only close relationship with soil characteristics, because the neutralization reaction with soil adherence is shown as:

$$\text{Soil-}(Al)_2 \cdot (OH)_2 + SO_4^{2-} \rightarrow \text{Soil-}(Al)_2 \cdot SO_4 + 2OH^-, \quad (1)$$

$$2OH^- + 2H^+ \rightarrow 2H_2O. \quad (2)$$

The tested soil distributed in southern China where weathering takes place rapidly under the high temperature and a great deal of precipitation. With the amounts of iron and aluminum oxide exist in kaolinite, the pH and basic saturation degree are low. The soil has been washed for a long time by acid rain, so the basic substances are very poor. The (ANC)c based on the carbonate and exchangeable base becomes lower in the soil. On the other hand, there are abundant non-Akira substance such as allophane in this soil, and amounts of sulfuric acid are adhered strongly by the iron and aluminum oxide in the soil, so (ANC)a based on soil adherence is very high. Therefore it can be assumed that the (ANC)a which adheres to the SO_4^{2-} in the precipitation, plays the role in the ANC of this soil, which is one characteristic of this kind of acid soil. In Japan, where is annoyed by the acid rain similarly, the minimum, maximum average values of ANC were 0.3 meq/100 g, 87 meq/100 g and 7.6 meq/100 g in the top layer soil, respectively. ANC is 12 meq/100 g or more in Kanto region, and ANC is 5 meq/100 g or less within from Kansai to Chuugoku region. The strength of ANC is almost randomly distributed in other areas.

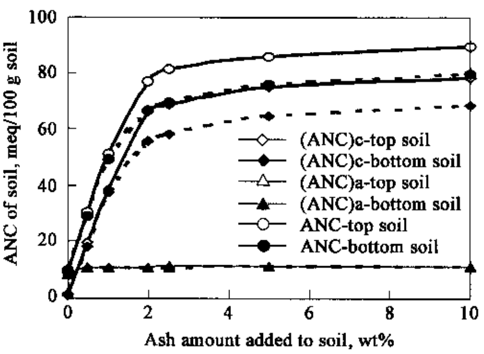

Fig.4 Effect of ash-addition on ANC of soil

The neutral-alkaline soils such as chestnut soil, sierozem, gray desert soil, drab soil, dark loessial soil, gray-drab forest soil and black soil are distributed in northern and northwestern China. The acidic soils and neutral-alkaline soils are divided across Yangzi River, and the ANC of the neutral-alkaline soils in northern and northeastern China is very different from that of acidic soil in southern China. There are large amounts of carbonate in northern and northwestern China, so(ANC)c plays the role in ANC with the assumption that ANC is controlled by(ANC)c in northern and northwestern China.

Fig. 4 shows that the changing tendency of(ANC)c has increased rapidly with the rise of the mixing ratio of the bio-briquette combustion ash. (ANC)c of the top layer soil was only 1.0 meq/100 g, it reached 67 meq/100 g when the tested soil was added with 2% of the combustion ash, and it is 10 times higher than that of the tested soil. Therefore, the acid-neutralizing capacity of the ash-added soil to acid deposition became stronger. Consumption of carbonate and exchangeable base in ash-added soil was carried out easily, because ratio of the cation and hydrogen ion in the improved soil solution was higher than that in tested soil. Therefore, although(ANC)a changed barely, the ANC increased rapidly in the ash-added soil.

Once more, Fig. 4 shows that the increasing tendency of ANC is obvious when mixing ratio of the combustion ash is below 2%, and the increase of ANC is gentle when mixing ratio of the combustion ash exceeds 2%. Therefore, if the mixing ratio of the bio-briquette combustion ash exceeds 2%, a stable acid-neutralizing capacity could be supplied to the improved soil.

3 Conclusions

In order to understand the improving effects in acidic soil with the addition of bio-briquette combustion ash, the study of the chemical and physical characteristics of the combustion ash-added soil is necessary. So the changes of acidity, *EC*, chemical characteristics and the acid-neutralizing capacity of the combustion ash-added soil have been studied widely. The effects of the bio-briquette combustion ash added to the tested acidic soil are summarized as follows.

The pH of tested soil is 4.19, and few effective elements(Ca, Mg, K, P and N) are in the soil, and Al and Mn ion concentrations are high, so the tested soil should be improved.

The contents of basic elements in the ash are very high, and there is a strong ANC to the acid deposition, and contents of heavy metal elements such as Al, Cu, Cd, Cr, Zn and Mn are almost the same level as the averages of them in Chinese soil, so it is deduced that the ash is possible as an additive to improve acidic soil.

When 5% of the ash was added, effective concentrations of Ca, Mg and K became about 100 times, 2 times and 7 times more than those of the tested soil, respectively. Also, the total nitrogen reached about twice higher than that of the tested soil. It is considered that the tested acid soil is returned to neutral-weak alkaline soil(pH 5.6—8.5) when 2%—8% of the ash is added to it.

It can be said that(ANC)a, which adheres to the SO_4^{2-} in the precipitation, plays an important role in ANC of the acidic soil. This is one characteristic of this kind of acid soil. Although the(ANC)a hardly changes, the ANC increases rapidly when the bio-briquette combustion ash is added to the tested soil.

pH and *EC* of the improved soil became high. And the experiment results suggested that the best mixing ratio of the bio-briquette combustion ash to the acid soil used in our study is 2.5%—8%.

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