The novel properties of a new inorganic water-retaining product made from coal fly ash

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Abstract

To utilize the huge amount of coal fly ash (CFA) in China and also address the challenge of drought whether in part area of China, a CFA comprehensive utilization as water-retaining product was proposed in this paper. In order to increase the CFA's water-retaining efficiency, a special process was adopted to re-generate and improve the micro-structure of CFA. As a result, it has a very high porosity of 80~90% and thereof it can absorb water as much as ~4 times of its own weigh. Meanwhile, the elements such as Si, Fe, Ca, Mg, S, etc, which exist in the original CFA are activated enough via this process. Particularly, it contains very high active silicon of more than 14%, far higher than the 3% of the original CFA. These activated elements are very beneficial to plants' growth. To explore the new product's effects on the plants in the arid area, a series of field tests have been carried out in 2017 and 2018. The results revealed that potato and corn yields are quite higher than the blank control groups by a tremendous rate.

Key words: coal fly ash, water-retaining, beneficial element, plant growth

1 Introduction

Coal Fly ash (CFA), a solid residue produced in the coal-fired power stations [1], has been the urgent issue to be solved due to its huge amount and serious environment impact in China. Now its annual production is estimated to be more than 600 million tons [2]. Especially, half of the CFA is produced in the north of China, where the population density is relatively low and thereof it can not be completely consumed via the traditional ways, such as brick, cement, concrete, etc [3-5]. That inevitably leads to a large amount of the CFA accumulation. Therefore there is an urgent need to develop more and new methods to utilize CFA more effectively and profitably.

North China is in the arid and semi-arid area, where water resource shortage is very serious. For example, in Xilinguole League, Inner Mongolia, the annual rainfall is only 150-350 mm, but annual evaporation reaches the value of 2000-2700 mm, as leads to the typical ecological environmental problems such as grassland degradation, land salinization and soil desertification, etc. But as one of the Chinese important lignite production and electric generation bases, not only a large amount of fresh water is consumed, but also a large amount of CFA is generated in Xilinguole League. So the areas like Xilinguole League are facing a severe environmental challenge.

To address the crisis of water resource shortage, many studies have been carried out. Among of these studies, developing water-retaining products is a research hot topic. Currently, super absorbent resins [6], such as starch grafting acrylic acid [7] or cellulose graft copolymer [8], etc, have been developed well. But they are not cheap and/or biocompatible, as limits their applications in the agriculture in a large scale. In contract, inorganic water-retaining product is more popular due to its lower production cost and good biocompatibility [9]. For example, because there are many water-absorbing hydroxyls on the surface of clay minerals and the clay minerals have layered structure，they have become the representative of inorganic water-retaining materials and thereof gone into our life.

As is well known, CFA is produced by the transformation of clay minerals in the coal during the process of combustion of the coal [10]. Its porous structure is often used to make CFA a water-retaining product, but its water-retaining efficiency is not high enough [11]. The major components of CFA are alumina and silica, which are very similar to that of the nature clay. In general, the contents of alumina and silica in CFA are about 20-40% and 40-60%, respectively [12]. And the main phases of CFA are mullite, quartz and/or amorphous silica depending on the variety of the raw coal and the combustion temperature of the coal-fired boiler. Moreover, there is a small amount of ferrite, calcium oxide, magnesium oxide, sulfate, and so on in the CFA. These components are not chemically steady, and they can be transformed under some specific conditions.

In view of above aspects, this paper will explore the transformation of CFA from a by-product during a combustion process at ~1200 ºC to an artificial clay-like material with high water-retaining capacity during a special process. Then, the water-retaining properties of this new product will be discussed subsequently in detailed. Simultaneously, considering silicon, calcium, ferrous and magnesium are very abundant in the CFA and these elements are beneficial to many plants' growth, a series of field tests including planting potato and corn have been carried out. So the problem of how much variation in the plant yield caused by such elements from the original CFA will be involved in this paper.

2 Materials and methods

2.1 Raw materials and apparatus

Coal fly ash was obtained from a coal fired power plant in Inner Mongolia, China. Sample of CFA was placed in an oven at 105 °C for 24 h for detailed analysis.

Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, PE Optima 5300DV, Perkin-Elmer) and Inductively Coupled Plasma–Mass Spectrometry (ICP-MS, iCAPQc) were used to analyze solid chemical composition of the CFA and plants. The phase of the equilibrium solid was identified by X-ray diffraction (XRD, Philips PW226/30 with Cu Kα radiation, 40 kV, and 100 mA). Morphology and mineralogical analyses were conducted using scanning electron microscope (SEM, JEOL 5800SV). Particle size distribution analyses were carried out on Mastersizer 2000 (Malvern). The available silica, calcium, magnesium contents in the CFA and the water-retaining products were determined with ICP-OES analysis recorded in *NT/T 2272-2012 soil conditioner* [13].

2.2 Experimental methods

To synthesize the water-retaining product from CFA, CFA was first modified by a special method. Then the modified CFA was characterized by the above apparatus.

In order to assess the effects of modified CFA on the plants' growth, we planted corn in three plots with 5 *mu* (667m^2 per *mu*), 5 *mu* and 7 *mu* in 2017 and 2018, respectively, and potato in one plot with 1 *mu* in 2018. The modified CFA was added combined with 25kg/*mu* N-P-K compound fertilizer by 50, 80, 100 kg/*mu*, respectively, when corn is sowing, while potato is changed to the condition of 100 kg/*mu* N-P-K compound fertilizer and 50 kg/*mu* modified CFA.

At harvest, at least five set of seed yield data every plot were collected and then the seed yield of each plant per *mu* was calculated. What needs to be added is that every seed yield data came from ten plants. For each kind of plant, the following measurements and observations were also made: seed of ten representative plants to analyze the heavy metals' contents and some pictures of plants' growth.

2.3 Sample analyses

To determine available beneficial element content in dried samples, ICP-OES analysis was conducted and the operation procedures were listed in *NT/T 2272-2012 soil conditioner*. ICP-MS was used to analyze the heavy metals' content in the plant. X-ray diffraction was used to identify solid phases. Scanning Electron Microscope was used to conduct morphology and mineralogical analyses. Mastersizer 2000 was used to test particle size distribution.

2.4 Plantation experiments

To test the activated CFA influence and the secondary and micro-elements uptake on plant growth, potato and corn were chosen for experiments because they are the main crops in the north of China. When exploring the effects of the activated CFA on the corn, three different soil types, castano-cinnamon soil, dark brown soil, and black soil, were chosen as the farming plots because they are the representative soil types in the north of China. The areas of the above three types of soil were 5*mu*, 5*mu* and 7*mu*, respectively. In each soil experiment plot, two blank control groups, fertilizer-free and traditional fertilization with 25 kg/*mu* N-P-K compound fertilizer, are set as comparison study. Meanwhile, in order to get the optimum amount of applied activated CFA in these three soils, different amount of 50, 80, 100 kg/*mu* combined with different amount of 15, 20, 25 kg/*mu* was experimented, respectively. In addition, three duplicates of each amount were conducted. When exploring the effects of the activated CFA on the potato, only one soil type, chestnut soil, was chosen as the farming plots since it is the representative soil type used to plant potato in the north of China. In this experiment plot, one blank control group, traditional fertilization with 100 kg/*mu* N-P-K compound fertilizer, was set as comparison study. For exploration study group, the addition of applied activated CFA was determined 50 kg/*mu*, reference to the proper activated CFA addition when planting corn in 2017, combined with the 100 kg/*mu* N-P-K compound fertilizer.

3 Results and discussion

3.1 Characterization of raw materials

The results of the chemical analysis of CFA are shown in **Table 1**, in the view of plant growth. They revealed that Al_2O_3, SiO_2, TiO_2, CaO and Fe_2O_3 were the principle components of CFA. The contents of Al and Si, the two key components, were found to be 11.37% and 25.93%, respectively, with a combined content of 37.30%. **Fig. 1** shows the particle size distribution (from 0.4 to 140μm) of the coal fly ash, with a volume average particle diameter of 13.43μm. The mineralogy phases of the coal fly ash were also examined, as shown in **Fig. 2**. The identified crystalline phases included Mullite ($Al_{1.69}Si_{1.22}O_{4.85}$), aluminum Oxide ($Al_2O_3$), and quartz ($SiO_2$). SEM images of the fly ash are shown in **Fig. 3**, revealing a smooth surface and sphere shape.

Table1 Chemical composition of coal fly ash

Macro- elements	N	P	K			
wt%	0.12	0.27	1.22			
Secondary elements	Si	Ca	Mg	S		
wt%	25.93	3.66	1.78	0.07		
Micro-elements	Fe	Mn	B	Cu	Zn	Cl

ppm, except Fe	4.8wt%	91.8	1128	61	163	0.23
Other elements	Al	Na				
wt%	11.37	1.05				

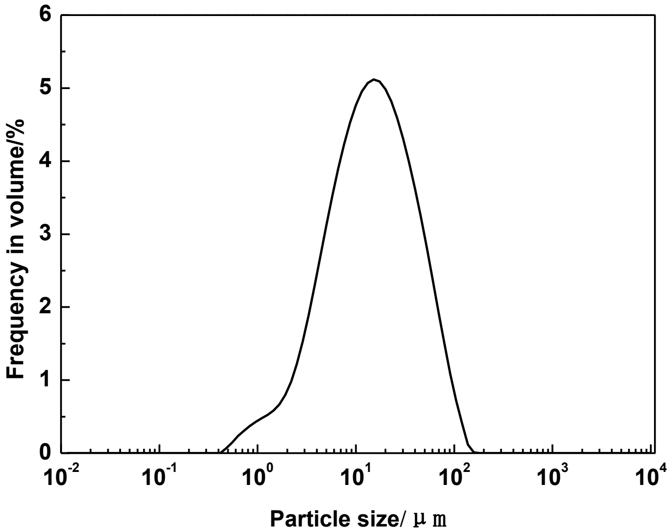

Fig.1 Particle size distribution of coal fly ash

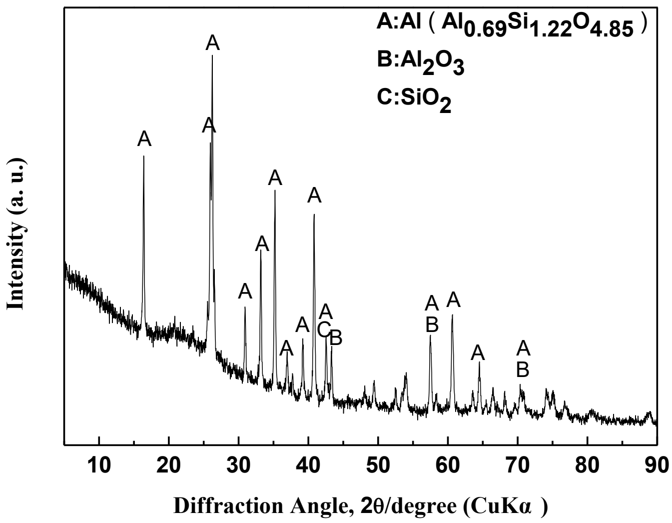

Fig.2 XRD pattern of coal fly ash

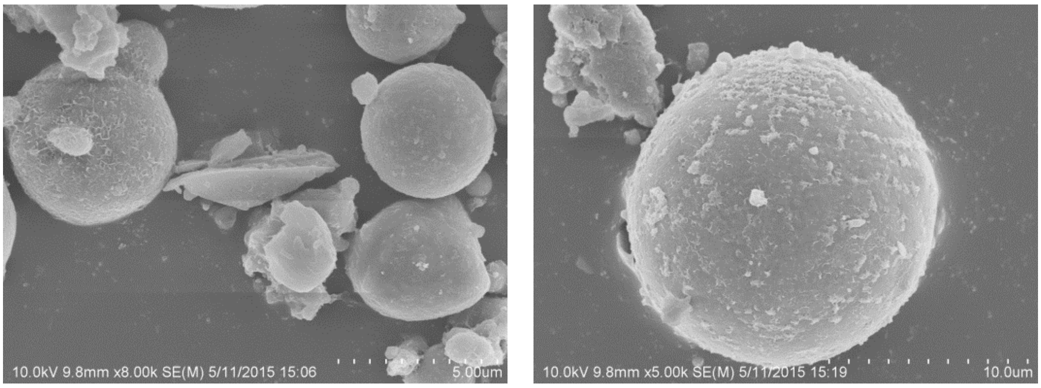

Fig.3 SEM images of coal fly ash

3.2 Properties of modified CFA product

After a series of experimental study, we have developed a new process to produce the water-retaining product using CFA as raw material. The main performance parameters comparison of CFA and the water-retaining product is shown in **Table 2**. Under the optimal conditions, the rate of available silica could reach 78.82% in the new water-retaining product, which is eight times higher than the value in CFA.

Table 2 The main performance parameters comparison of CFA and the water-retaining product

Available content rate, %	SiO_2	CaO	MgO	Fe_2O_3	K_2O
CFA	9.35	60.23	44.80	37.50	7.62
Water-retaining Product	78.82	96.90	43.28	57.60	43.41

Note: available content rate= available content of an element / total content of an element

3.3 Results of field experiments

In order to verify the actual yield-increasing performance of the water-retaining product, we began to conducted field experiments on the product from 2017. Three different soil types of castano-cinnamon soil, dark brown soil and black soil were chosen as the experimental soils for corn planting and chestnut soil was chosen for potato planting. The specific geographical location of the test fields are shown in Fig. 4. "▲" is the black soil field for corn planting, whose area is 7 *mu*, and "●" are also for the corn planting, 5 *mu* castano-cinnamon soil and 5 *mu* dark brown soil fields. "◆" is the chestnut soil field for potato planting, about 1 *mu*.

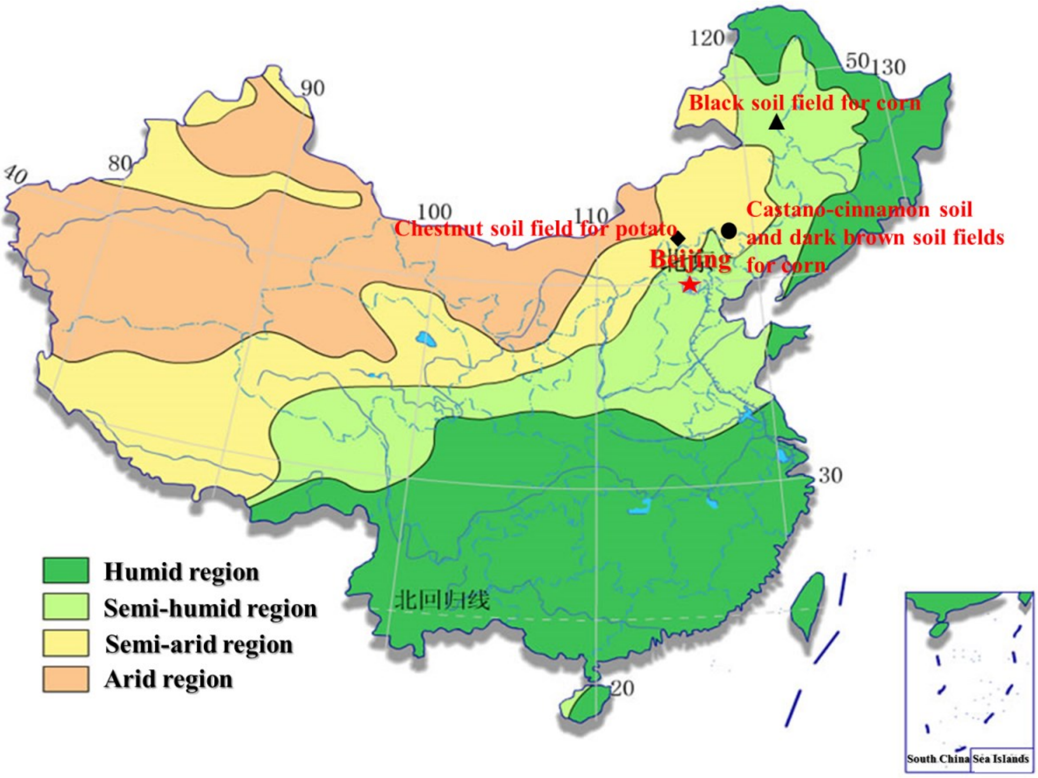

Fig. 4 The specific geographical location of the test fields

Some of the field experiments photos were shown in **Fig. 5** for corn and **Fig.6** for potato.

The photos in **Fig. 5** were arranged in chronological order. It can be seen that the plumping corn seeds have been achieved.

Fig. 5 Some of the field experiments photos for corn

Fig. 6 Some of the field experiments photos for potato

The left photo in **Fig. 6** revealed that the aerial stem colors of blank control group and exploration study group at harvest are quite different. The former has turned yellow, and the latter still green. The middle photo in **Fig. 6** showed that potato fruits under applying the activated CFA conditions grew well, some of them are as long as 16 cm. The right photo in **Fig. 6** showed that, on the whole, potato fruits under applying the activated CFA conditions are bigger and have a better quality than that in blank control group.

3.3.1 Corn field experiments

3.3.1.1 Corn planted in castano-cinnamon soil for 2017 and 2018

The yield data of corn planted in castano-cinnamon soil for 2017 and 2018 were shown in **Table 3** and **Table 4**, respectively.

Table 3 The yield data of corn planted in castano-cinnamon soil for 2017

Groups	Average weight of ten corn plants /kg	Average yield per mu /kg	Yield-increase rate 1 /%	Yield-increase rate 2 /%
Blank Control (BC)	2.32	717.57	0.00	-1.18
Conventional Fertilization(CF)	2.35	726.15	1.20	0.00
CF+ Water-Retaining Product(WP)	2.56	789.67	10.05	8.75
80% of CF+WP	2.59	801.68	11.72	10.40
50% of CF+WP	2.58	798.25	11.24	9.93
80% of CF+50% of WP	2.59	799.97	11.48	10.17

Note: Yield-increase rate 1 and Yield-increase rate 2 are based on blank and conventional fertilization, respectively.

Table 4 The yield data of corn planted in castano-cinnamon soil for 2018

Groups	Average weight of ten corn plants /kg	Average yield per mu /kg	Yield-increase rate 1 /%	Yield-increase rate 2 /%
Blank Control (BC)	1.183	468.9	0.00	-8.27
Conventional Fertilization(CF)	1.302	511.2	9.02	0.00
CF+ Water-Retaining Product(WP)	1.467	582.3	24.18	13.91
80% of CF+WP	1.450	572.4	22.07	11.97
50% of CF+WP	1.983	778.3	65.98	52.25
80% of CF+50% of WP	1.381	543.9	15.99	6.40

Note: Yield-increase rate 1 and Yield-increase rate 2 are based on blank and conventional fertilization, respectively.

From the above tables it can be seen that the water-retaining product played a great role in increasing corn production in castano-cinnamon soil for both 2017 and 2018. In 2017, contrasting with the conventional fertilization group, the highest yield of corn would be rose by 10.40% and the amount of conventional fertilization could be reduced 20%. In 2018, in comparison to the conventional fertilization group, the highest yield of corn would be rose by 52.25% and the amount of conventional fertilization could be reduced 50%.

3.3.1.2 Corn planted in dark brown soil in 2017 and 2018

The yield data of corn planted in dark brown soil for 2017 and 2018 were shown in **Table 5** and **Table 6**, respectively.

Table 5 The yield data of corn planted in dark brown soil for 2017

Groups	Average weight of ten corn plants /kg	Average yield per mu /kg	Yield-increase rate 1 /%	Yield-increase rate 2 /%
Blank Control (BC)	1.71	684.00	0.00	-3.99
Conventional Fertilization(CF)	1.78	712.44	4.16	0.00
CF+ Water-Retaining Product(WP)	1.81	725.78	6.11	1.87
80% of CF+WP	1.79	715.11	4.55	0.37
50% of CF+WP	1.83	732.44	7.08	2.81
80% of CF+50% of WP	1.86	744.44	8.84	4.49

Note: Yield-increase rate 1 and Yield-increase rate 2 are based on blank and conventional fertilization, respectively.

Table 6 The yield data of corn planted in dark brown soil for 2018

Groups	Average weight of ten corn plants /kg	Average yield per mu /kg	Yield-increase rate 1 /%	Yield-increase rate 2 /%
Blank Control (BC)	1.486	520.5	0.00	-8.33
Conventional Fertilization(CF)	1.621	567.8	9.09	0.00
CF+ Water-Retaining Product(WP)	1.801	620.4	19.19	9.26
80% of CF+WP	1.743	608.4	16.89	7.15
50% of CF+WP	1.742	613.4	17.85	8.03
80% of CF+50% of WP	1.809	634.0	21.81	11.66

Note: Yield-increase rate 1 and Yield-increase rate 2 are based on blank and conventional fertilization, respectively.

As shown as in the above tables, it can be conducted that the water-retaining product also played important role in promoting corn production in dark brown soil for both 2017 and 2018. In 2017, under 80% of CF+50% of WP fertilization condition, the corn yield increased 4.49% and 8.84% respectively than the conventional fertilization group and blank control group. In 2018, as same as the result of 2017, the 80% of CF+50% of WP group gave highest yield. It was shown that the highest yield would be rose by 11.66% and the amount of conventional fertilization could be reduced 80%, meanwhile, the amount of water-retaining product could be reduced 50%.

3.3.1.3 Corn planted in black soil for 2017 and 2018

The yield data of corn planted in black soil for 2017 was shown in **Table 7**.

Table 7 The yield data of corn planted in black soil for 2017

Groups	Average weight of $6.5m^2$ /kg	Average yield per mu /kg	Yield-increase rate /%
Conventional Fertilization(CF, 30kg/*mu*)	7.35	753.9	0.00
80% of CF + Water-Retaining Product(WP,100kg/*mu*)	10.35	1061.6	40.81
80% of CF+80% of WP	10.45	1071.9	42.18
80% of CF+50% of WP	9.75	1000.1	32.66
60% of CF+WP	9.20	943.6	25.16
60% of CF+80% of WP	8.50	871.8	15.64
60% of CF+50% of WP	7.85	805.2	6.80

Note: Yield-increase rate is based on conventional fertilization.

The results shown in the above table indicated that the water-retaining product made a better role in increasing the yield in black soil than in castano-cinnamon soil and dark brown soil. In 2017, the 80% of CF+80% of WP group gave the highest yield which was rose by 42.18% compared to the conventional fertilization group. What's more, even in the 60% of CF+50% of WP group, it also got a 6.80% increase in yield.

In 2018, our experiment filed suffered serious floods unfortunately. This led to the distortion of yield data, so the data of 2018 were not provided here. We have already made the planting plan this year to repeat last year's experiment design.

3.3.2 Potato field experiment

The yield data of potato planted in chestnut soil for 2018 was shown in **Table 8**.

Table 8 The yield data of potato planted in chestnut soil for 2018

Group	Sampling Number	Fruit Number	Weight /kg
Conventional Fertilization(CF)	15	102	12.2
CF + Water-Retaining Product(WP)	13	75	14.0

As seen from **Table 8**, after applying the water-retaining product, the yield of potato had a significantly improvement. When adding the water-retaining product, the average weight of single potato is 56% higher than that under the conventional fertilization conditions. And the yield data was 14.8% higher than later, reaching the level of near 3500 kg/*mu*.

3.3.3 Detection of heavy metals contents

The potential harms of heavy metals in CFA is a hot issue when CFA is used for agriculture. So the accurate quality examinations to all the corn and potato samples were conducted after the harvest. And part of the examination results were shown in **Table 9** for corn and **Table 10** for potato.

As shown in **Table 9** and **Table 10**, it can be seen that there was no significant increase of heavy metals content in corn and potato products after applying water-retaining product. And quality of corn and potato products after applying water-retaining product can fully meet the Chinese and European Union standards. Certainly, the continuous tracking detection is still a must-do as well.

Table 9 The content of heavy metals in corn fruit after applying water-retaining product

Elements	Pb	Cd	Hg	As	Cr
Detection Limit mg/kg	0.02	0.001	0.003	0.010	0.001
Blank Control (BC)	/	/	/	/	0.450
Conventional Fertilization(CF)	/	/	/	/	0.399
CF+ Water-Retaining Product(WP)	/	/	/	/	0.213
80% of CF+WP	/	0.001	/	/	0.187
50% of CF+WP	/	/	/	/	0.190
80% of CF+50% of WP	/	/	/	/	0.230
China food safety standard of GB 2762-2012	0.2	0.1	0.02	0.5	1.0
European food safety standard of EC 1881/2006	0.2	0.1	/	/	/

Table 10 The content of heavy metals in potato fruit after applying water-retaining product

Elements	Pb	Cd	Hg	As	Cr
Detection Limit mg/kg	0.02	0.001	0.003	0.010	0.001
Conventional Fertilization(CF, 100 kg/*mu*)	/	/	/	/	0.031
CF+ Water-Retaining Product(WP, 50 kg/*mu*)	/	/	/	/	0.043
China food safety standard of GB 2762-2012	0.2	0.1	0.02	0.5	1.0
European food safety standard of EC 1881/2006	0.2	0.1	/	/	/

4 Conclusion

A new inorganic water-retaining product was synthesized successfully from coal fly ash and a series of field experiments research were carried out to verify its yield-increasing effect. The main conclusions can be drawn as follows:

1）In synthesized process, large amount of Si element and other beneficial elements were activated. The content of available silica in the water-retaining product could reach 14.29% which is much higher than in CFA of 2.79%.

2) By conducting field experiments in different types of soil and crops, it was found that water-retaining product had an extensive adaptability. For corn planted in castano-cinnamon soil and dark brown soil, higher than 10% increase in corn yield was obtained upon adding this water-retaining product. And in black soil, a tremendous yield-increasing rate of 42.18% was accomplished. Meanwhile, it also can reduce the dosage of chemical fertilizer to some extent.

3) The quality examination results of the corn and potato samples confirmed that no significant increase of heavy metals content in fruit after applying water-retaining

product and they can fully meet the Chinese and European Union food standard requirements.

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