Fly Ash-based Technologies and Value-added Products Based on Materials Science

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KEYWORDS: fundamental properties, fly ash-based products, fillers, flame retardants, geopolymer foams, low carbon specialty ready-mix mortar, low carbon cement

ABSTRACT

China generates more than 50% fly ash volume globally since 2008 and reaches 520 million tons in 2013, but is not expected to exceed 600 million tons in 2020 due to the maximum total coal consumption of 4.2 billion tons set by the Chinese government. Even though the China's utilization rate has been steadily increased to 68-70% higher than the global average (54%), the un-utilized volume is also gradually increased to 170 million tons. How to fully utilize fly ash is still a challenging issue in China, particularly for those power plants located in remote areas. The main issues are massive volume and significant variations in 3 fundamental properties: particle size and its distribution, chemical compositions, and mineral compositions. How to efficiently "transform" fly ash produced from each power plant into the desired consistent-quality raw material is the first scientific challenge. Then, how to effectively utilize consistent-quality fly ash to develop and commercialize core technologies and value-added products for selected applications is the second important challenge.

This paper demonstrates the approaches that scientists at NICE, a subsidiary of Shenhua Group as one of the world largest coal producers, develop core technologies to transform coal fired power plant fly ashes into consistent raw materials and to make value-added products based on materials science. Three core technologies have been developed to make 5 different types of fly ash-based products ranging from building and filler materials to high value flame retardants. The estimated market opportunity for these products in China is over ¥42 billion revenue and 50 million tons CO_2 reduction with the maximum fly ash consumption over 70 million tons. However, this is still not big enough to fully consume un-utilized fly ash volume over 170 million tons in China. Therefore, the scientific community needs to continue developing new products for new applications based on the existing core technologies, and developing new core technologies and products for new opportunities based on materials science concept and approach.

INTRODUCTION

China is the second large energy user behind US in the world, and is expected to exceed US as the top energy consumer after 2015.[1] The primary energy resource is still fossil-based. Among fossil-based fuels, coal is more widely available but not as efficient as oil or natural gas to produce energy. The heat value is roughly 24 MJ/kg (6.67kW•h/kg) for coal, 47.2 MJ/kg (13.2 kW•h/kg) for oil, and 53.6 MJ/kg (15 kW•h/kg) for natural gas. According to the National Bureau of Statistics in 2010, China had the fossil-based energy reserves about 279 billion tons coal, 0.3174 billion tons oil, and 3.78 trillion cubic meters natural gas. Converting to the calorific value, the fossil-based energy reserves in China is about 95.4% from coal, 2.2% from oil and 2.4% from natural gas. China is a country rich with coal but lack of oil and natural gas.

Coal has two primary uses; one as direct combustion to produce energy in form of electricity or heat; the other for industrial uses to produce various materials, such as tar, coke, carbon blacks, fibers, synthetic fuels, iron and steel, and cement. At present, China uses about 50% of the total coal to produce electricity and heat which generate coal ash. Burning coal causes two environmental issues: 1) air pollution, such as NO_x, sulfur compounds, and CO_2 emissions, and 2) solid waste disposal, including fly ash, bottom ash, and desulfurized gypsum. Both have very serious environmental issues. On November 19, 2014, due to the change in energy supply structure and increasingly stringent environmental policy, China's State Council has set the limit of coal consumption no more than 4.2 billion tons in 2020. Figure 1 shows the historical total coal consumption and amount used to generate electricity and heat from 2000 to 2013 and the projected values in 2020.

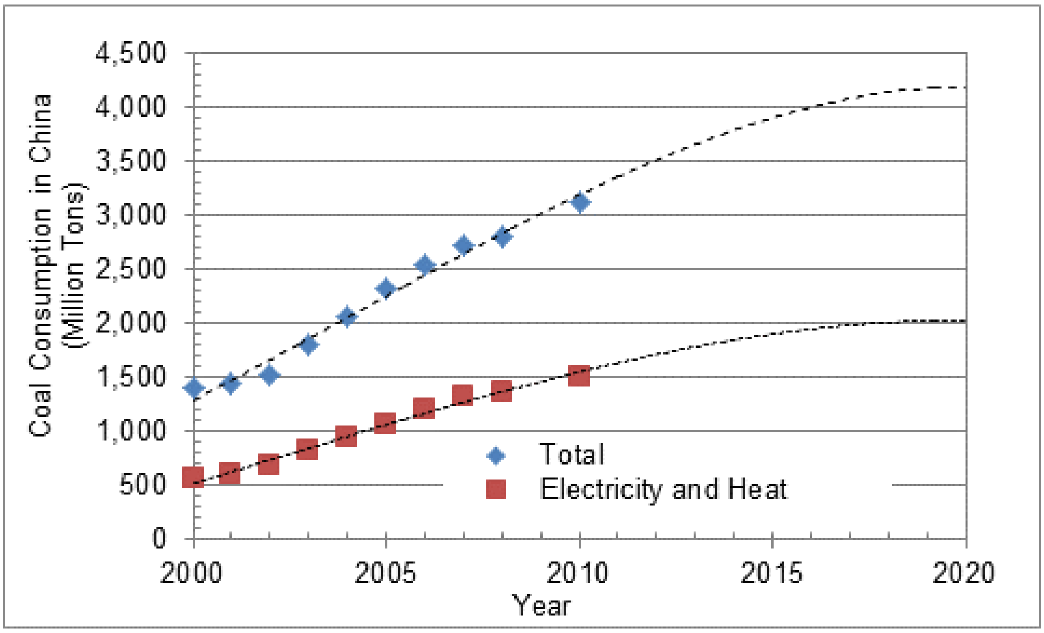

Figure 1 Total coal use and use for electricity and heat in China from 2000 to 2013

Figure 2 shows % of historical coal uses in 4 areas, electrical and heat, coal chemicals, other industry use, and non-industry use from 2000 to 2012 and the expected percentages from 2012 to 2020: 50 to 56%, 15 to17%, 30 to 26%, and 5 to 1%, respectively. Obviously, electricity and heat are the major uses, and they continue to grow along with coal chemicals. Fly ash is one of top solid wastes in China as listed in Table 1, and includes ash from industry boilers as well as bottom ash.

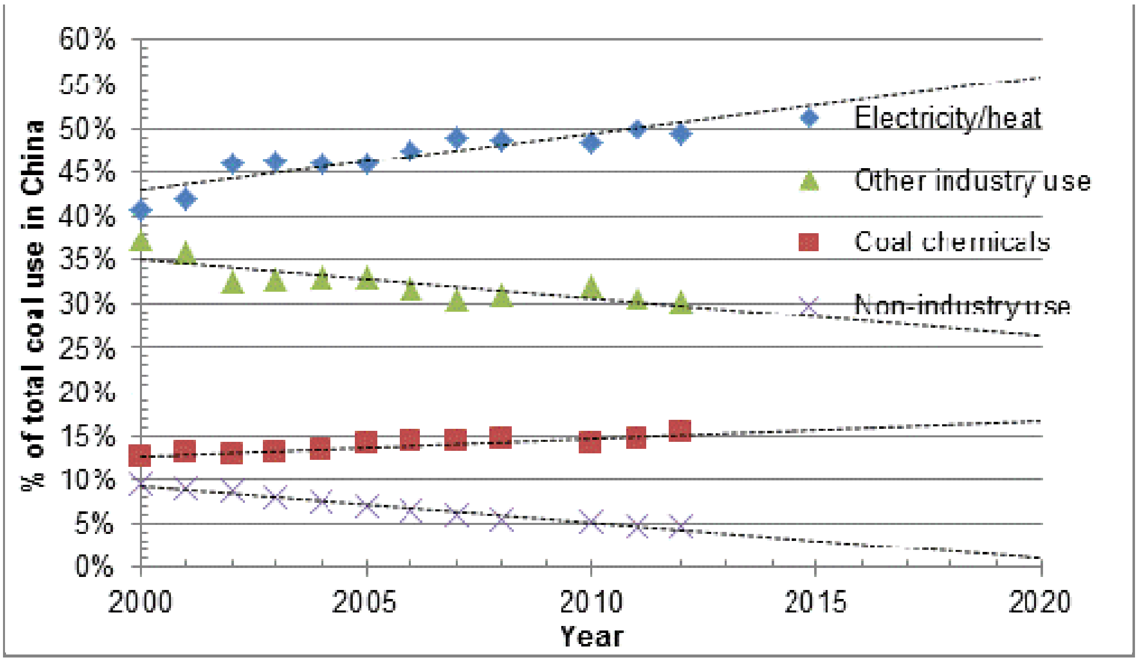

Figure 2 Historical and predicted % coal utilization in 4 major areas

Table 1 Massive industrial solid waste status and utilization in China

Types/Year Unit: million tons	Production		Utilization		Utilization rate	
	2005	2010	2005	2010	2005	2010
Tailing	714	1214	50	170	7%	14%
Coal Gangue	370	598	196	365	53%	61%
Fly ash	301	480	199	326	66%	68%
Smelting slag	180	317	90	190	50%	60%
Gypsum	50	125	5	50	10%	40%
Red mud	10	30	0.2	1.2	2%	4%
Total	1,625	2,764	540.2	1102.2	33%	40%

The annual production and utilization of fly ash in China from 2000 to 2013 and the projected values in 2020 are shown in Figure 3. Fly ash is significantly increased due to significant energy demands with fast growing in coal consumption for electricity and heat. Based on historical total coal consumption and % used for producing electricity and heat, the quantity of fly ash is about 14% of total coal consumption or 30% of coal used for electricity and heat. Therefore, the total volume will not exceed 600 million tons in 2020.

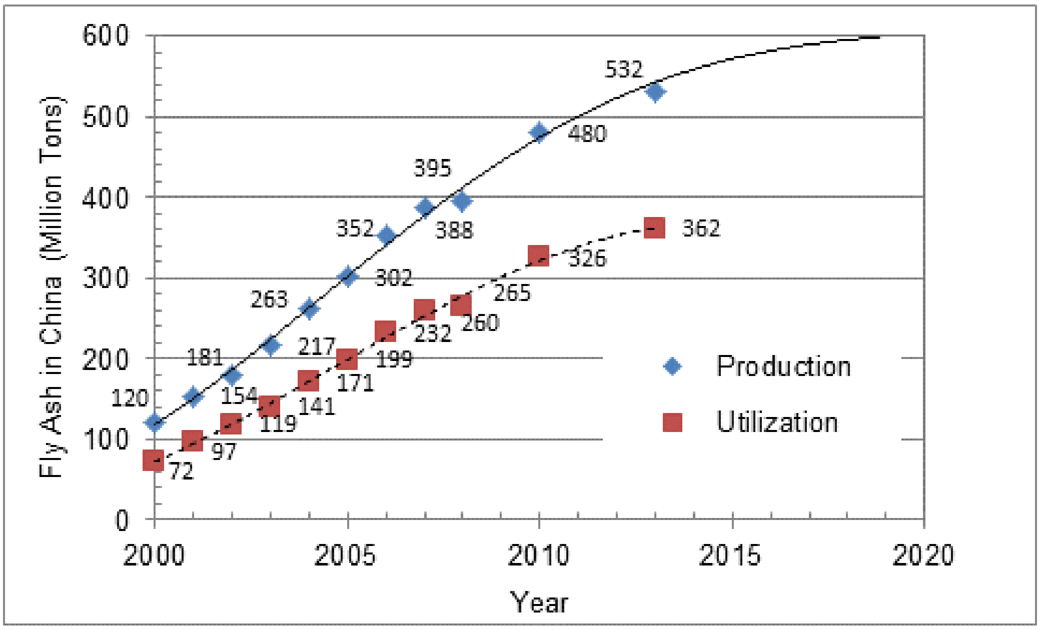

Figure 3 Annual fly ash production and utilization from 2000 to 2013 in China

Table 2 Global fly ash production and utilization rate in 2008

Country	Quantity （Million tons）	Share (%)	Utilization rate (%)
China	395	51%	67%
USA	118	15%	42%
India	105	14%	13%
EU (15 countries)	53	7%	91%
Africa and Middle East	32	4%	11%
Russia	27	3%	19%
Other Asia countries	17	2%	67%
Australia	13	2%	46%
Japan	11	1%	96%
Canada	7	1%	34%
Total	777	100%	54%

China has produced more than 50% fly ash globally since 2008 as listed in Table 2. Even though the utilization rate in China was higher than the global average (67% vs. 54%), the un-utilized fly ash volume has been significantly increased annually. The annual un-utilized volume was from 48 million tons in 2000, 102 million tons in 2005,154 million tons in 2010 to 170 million tons in 2013, and is expected to reach 174 million tons in 2015 at the 70% utilization rate. If the utilization rate is still 70% in 2020, the un-utilized fly ash amount will be 180 million tons. The un-utilized fly ash volume in China since 2013 has been higher than the total fly ash volume produced in the second global largest fly ash produced country, USA. Therefore, a significant change in the current utilization mind-set and approach is needed in order to reduce un-utilized volume or reach fully utilization which is critical to China for social and economic aspects.

In 2013, the Chinese National Development and Reform Commission revised its regulation of fly ash utilization management with the principle of “who produce, who manage, and who take advantage of benefits” and no more than 3-years fly ash storage capacity for any new coal-fired power plant only if needed.[2] Full fly ash utilization is becoming the trend and will be a must, particularly for a new power plant. Another trend in China is to build new mega coal-fired power plants in the remote industry parks nearby coal mines, and transmit electricity from remote to urban areas or from west to east regions. Therefore, how to fully utilize fly ash from each coal-fired power plant, particularly located in a remote area, is the most critical and challenging task in China.

FUNDAMENTAL SCIENCES BASED FLY ASH UTLIZATION

Why not every single coal-fired power plant has its fly ash fully utilized? The common reasons are due to power plant location, massive volume, and significant property variations from plant to plant or even from time to time at the same plant. Depending on the designed electricity capacity, each coal-fired power plant could produce fly ash in several ten thousands to a few million tons. In general, 1 kW capacity produces 0.5 ton fly ash annually. Due to massive fly ash volume with significant property variations, the major utilization is in local low-value high-volume buildings and constructions which are typically limited to 100 km utilization distance due to the transportation cost. Therefore, depending on the power plant location, fly ash produced from the coal-fired power plant nearby metropolitan areas or along east coast regions can be easily fully utilized for the local buildings and constructions due to fast and massive local infrastructural growth. However, for those plants located in remote areas or inner land regions, fly ash is always under-utilized due to low local building and construction demands. For example, one thermal power plant located at Sanhe within the Hebei providence owned by Guohua Power Company as a subsidiary of Shenhua Group produces about 400,000 tons fly ash each year, and has 100% utilization due to the location nearby Beijing and Tianjin metropolitan areas. But another power plant located in the northwestern region of China within the Shaanxi providence annually produces 600,000 tons fly ash and has only 30-40% fly ash utilized into local buildings and constructions during summer, and the rest is landfilled.

The current fly ash utilization in China is categorized into 5 areas (and their percentages): cement and concrete (60%), bricks and walls (26%), road and road pavement (5%), agriculture and refilling (5%), and high-end applications including mineral extraction (4%). The first three areas for buildings and constructions have about 91% of the total utilization. The first 4 utilization areas have about 96% of the total utilization as local low-value applications. The high-end utilization is still very low at only 4%. The current overall utilization rate in China has reached the level of 68 - 70%. The full utilization is still far to reach unless fly ash from each coal fired power plant, particularly located in a remote area, can be fully utilized.

To fully utilize fly ash with large volume from any coal-fired power plant, particularly in a remote area, needs to identify and create sufficient needs in local and beyond local markets and to generate sufficient utilization value so that the solutions can be implemented to fulfill needs profitably to achieve the full utilization. Therefore, the key issue is the concept and approach of utilization: solid waste vs. materials science based value creation.

Solid waste utilization focuses on fast and massive utilization with high tolerance in property variation, resulting in massive local low-value utilization. For materials science utilization, fly ash is treated as a non-renewable resource, not a solid waste. So, firstly we need to characterize and understand fundamental and basic (physical and chemical) properties and the variations of fly ash produced from each power plant, and also need to be familiar with many applications and market needs related to these properties. Since fly ash has significant variations in its properties, we need to have the simple and effective method to “classify” fly ash into several classes of raw materials with consistent quality. With “classified” consistent-quality fly ash, we can develop core technologies to produce consistent value-added products required for selected applications most suitably and preferably based on its properties as well as the market needs relative to its power plant location. Thus these fly ash-based products can be designed to target various applications, particularly high value-added applications, by fully utilizing its fundamental and basic properties through the most cost-effective technologies to increase its value to reach its full utilization, and to maximize its utilization value for fly ash produced from each coal fired power plant, regardless of its location.

FUNDAMENTAL AND CHEMICLA/PHYSICAL PROPERTIES OF FLY ASH

Not all fly ashes are produced from the same combustion processes or using the same coal types or sources. Based on the coal combustion process, fly ash can be divided into: pulverized ash, circulating fluidized bed ash, industrial boiler ash, and gasification combined cycle ash. Figure 4 is a pulverized coal-fired power plant. But every fly ash has the same 3 fundamental properties: particle size and its distribution, chemical compositions, and mineral compositions, related to its physical and chemical properties. The variations in these fundamental properties are directly related to its coal source, coal pretreatment, combustion process, and dust collection system.

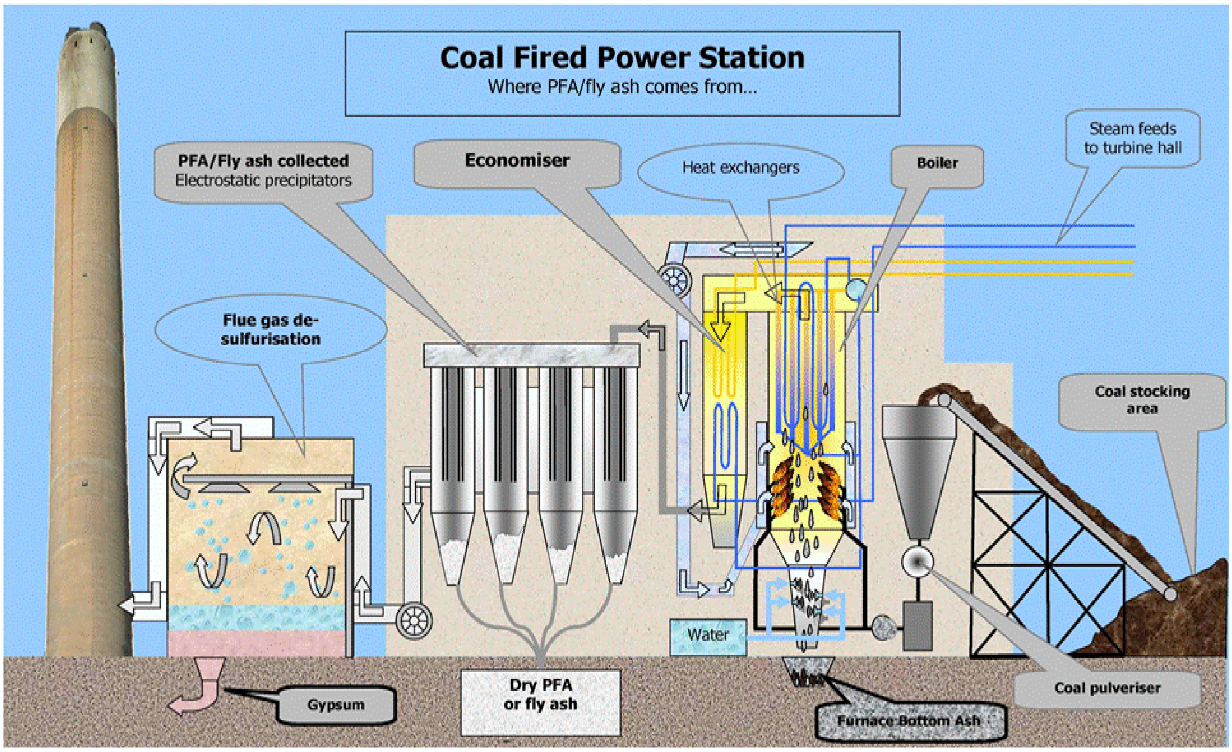

Figure 4 Typical pulverized coal-fired power plant

Particle size and its distribution of fly ash depend on the coal pretreatment, combustion processes, and ash collection system. In general, fly ash has the particle size range from 0.1 to 600 μm. Fine coal particle produces finer fly ash. Fly ash at the same plant collected at different electrostatic precipitator has different average particle size; the farther precipitator, the smaller average particle size. Chemical compositions depend on coal type (such as anthracite, bituminous coal, sub-bituminous coal, or lignite) and extent of combustion. Burning a low rank coal such as lignite or sub-bituminous coal usually produces fly ash with high CaO content. All fly ashes have 2 major chemical components, SiO_2 and Al_2O_3 as an aluminosilicate material, and 4 secondary components, CaO, Fe_2O_3, SO_3, and unburned carbon (Loss of Ignition, LOI). It also has several minor components (<5%), such as K_2O, MgO, Na_2O, and TiO_2, and many trace amounts (< 0.1%) of other oxides, including heavy metals. Mineral compositions depend on coal type, coal particle size, boiler temperature, and ash cooling and collection systems. In general, higher temperature of the boiler and the smaller coal particles produce fly ash with higher glass content and lower LOI. For mineral compositions, fly ash typically has glass content from 35 to 70%. The typical mineral crystals include two major minerals, mullite ($Al_6Si_2O_{13}$) and quartz (SiO_2), and other minor minerals, such as hematite (Fe_2O_3), magnetite (Fe_3O_4), lime (CaO), anhydrite ($CaSO_4$), anorthite ($CaAl_2Si_2O_8$), and periclase (MgO). High CaO fly ash has high lime content and additional Ca-containing mineral crystals, such as tricalcium aluminate ($Ca_3Al_2O_6$) and gehlenite ($Ca_2Al_2SiO_7$). High Al fly ash typically has higher Al content in form of mullite and corundum (Al_2O_3) in crystal phase. Therefore, high Al fly ash may not necessarily have higher amorphous Al_2O_3 content than low Al fly ash.

Figure 5 shows how 3 fundamental properties of fly ash can be related from its coal-fired power plant and to its physical and chemical properties. Core technologies and value added products will be developed based on its unique properties.

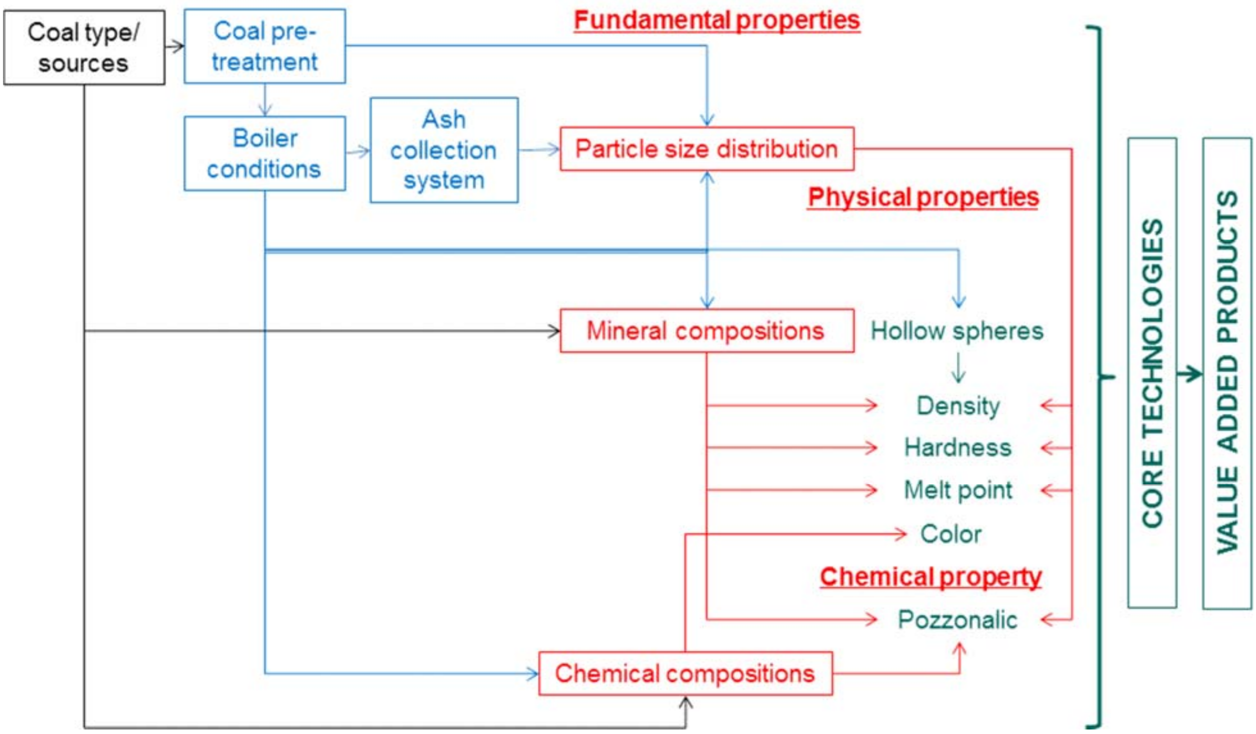

Figure 5 from coal combustion to fly ash properties for core technologies and products

The most unique physical property of fly ash is its sphere shape as shown in Figure 6 due to high temperature melting and cooling in the combustion process. Density, hardness, and melt temperatures are also related to particle size and mineral compositions with the typical range of 2.15 – 2.30 g/cc, 5 – 6 Mohs, and 1200 - 1400°C, respectively for a pulverized ash. Key fly ash chemical property is pozzolanic reactivity which is related to Si and Al in glass phase (chemical and mineral compositions) and surface area (particle size distribution), while fly ash with high CaO can also have cementitious reactivity. The color of fly ash is typically grey, but can be different due to certain chemical compositions; light grey for high Al_2O_3, yellowish for high CaO, brownish to reddish for higher iron oxide content, and dark gray to black for high LOI.

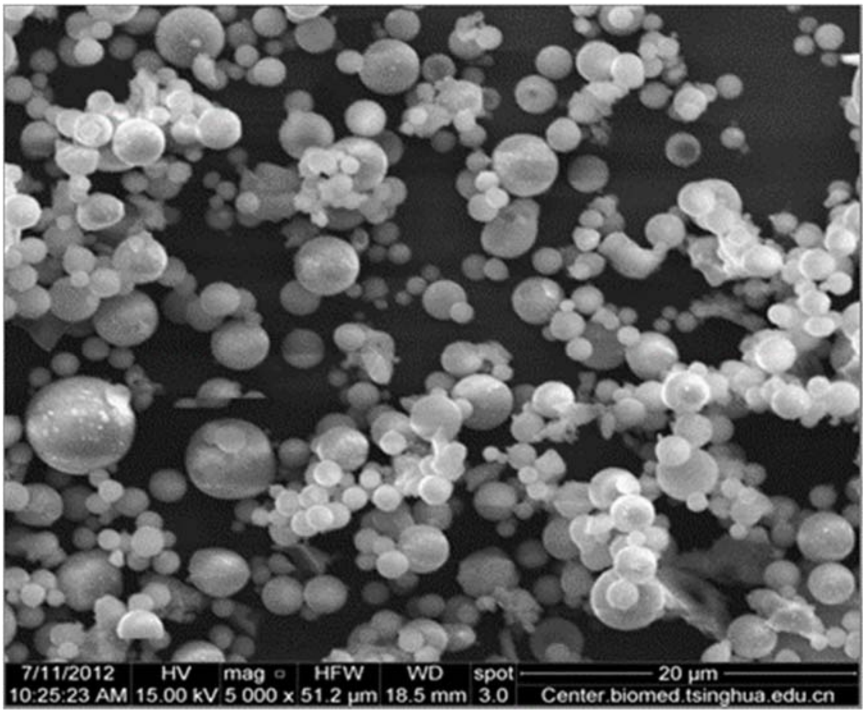

Figure 6 Fly ash SEM

Particle size and its distribution can be measured by a laser particle size analyzer (Malvern mastersizer 2000) using water as a dispersant. Chemical compositions except LOI are measured by the XRF method using A Rigaku fully automated sequential X-ray Spectrometer, while LOI is measured according to GB/T 176 using a combustion oven procedure. Mineral compositions are measured by X-ray diffraction (XRD) using Rigaku RINT2000 powder diffraction instrument under Cu Kα radiation, X-ray tube voltage of 40kV, tube current of 100mA, a scan rate of 2°/min, step width of 0.02 °, 2θ range of 5 ° ~ 70 ° continuous scan. The Jade 5.0 software is used to analyze the XRD patterns to match the location of each possible mineral crystal and determine the quantity of each mineral crystal and calculate the total degree of crystallinity.

Below are the examples of different fly ashes, identified as BJ, SH, CD, SZ, JJ, and ZG, from 6 Guohua's power plants, including fine and coarse fly ashes from CD and SZ identified as CD-f, CD-c, SZ-f, and SZ-c to compare their particle size distributions, chemical compositions, and mineral compositions. Certain applications have defined these requirements. For example, the Chinese national standard, GB1596-2005 “fly ash used for cement and concrete” as listed in Table 3, uses the particle size of 45 μm (or 325 mesh sieve) to classify fly ash fineness, and defines fly ash with no higher than 12%, 25%, or 45% by weight greater than 45 μm as Class I, II, or III fly ash, respectively. For chemical compositions, this standard also specifies LOI not higher than 5%, 8%, and 15% for Class I, II, or III fly ash, respectively. It also requires SO_3 no higher than 3%, and Ca^+ not higher than 1% for Class F fly ash or 4% for Class C fly ash. However, there is no direct requirement for mineral compositions, but it indirectly relies on Le Chatelier stability or strength activity index.

Table 3 GB/T 1596-2005 fly ash technical requirements used for cement and concrete

cement paste and concrete						active cement mix
Items	Class	Spec.	I	II	III	
fineness: > 45 μm	F or C	Max.	12%	25%	45%	N/A
LOI (Loss of Ignition)	F or C	Max.	5%	8%	15%	8%
Water demand	F or C	Max.	95%	105%	115%	N/A
Water content	F or C	Max.	1%			1%
SO_3	F or C	Max.	3%			3%
Ca^+ (Class F; CaO≤10%)	F	Max.	1%			1%
(Class C; CaO>10%)	C	Max.	4%			4%
Le Chatelier Stability	C	Max.	5/mm			5/mm
Strength activity index	F or C	Min.	N/A			70%

Figure 7 shows significant variations in particle size distributions for all these fly ashes. The particle size range is very wide from 0.2 to 850 μm. Figure 8 shows their accumulated volumes. Table 4 lists the particle size range, D_{50}, D_{90}, and wt% > 45 μm of these 8 different fly ashes.

These 8 fly ashes can be divided into 3 groups according to GB1596-2005 fly ash fineness definition: Group 1 for CD-f and ZG to meet Class I, Group 2 for JJ, BJ, SH, and SZ-f to meet Class II, and Group 3 for SZ-c and CD-c with no rating. Of course, there is another fly ash group to meet Class III fineness requirement. Different fly ash fineness can be defined according to each application need.

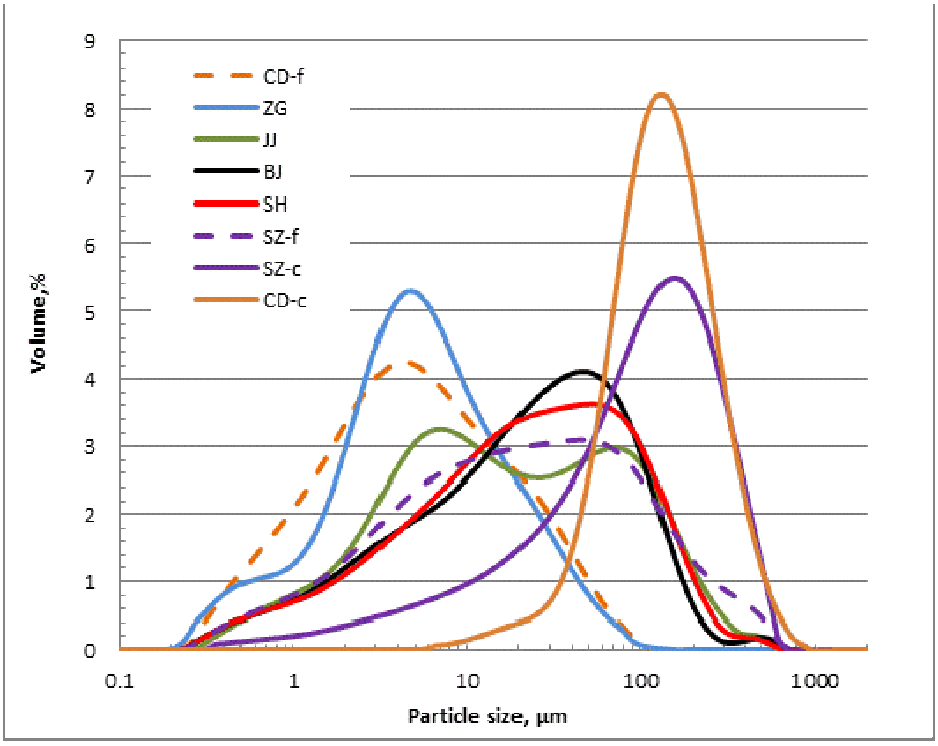

Figure 7 Particle size distributions of 8 fly ash samples

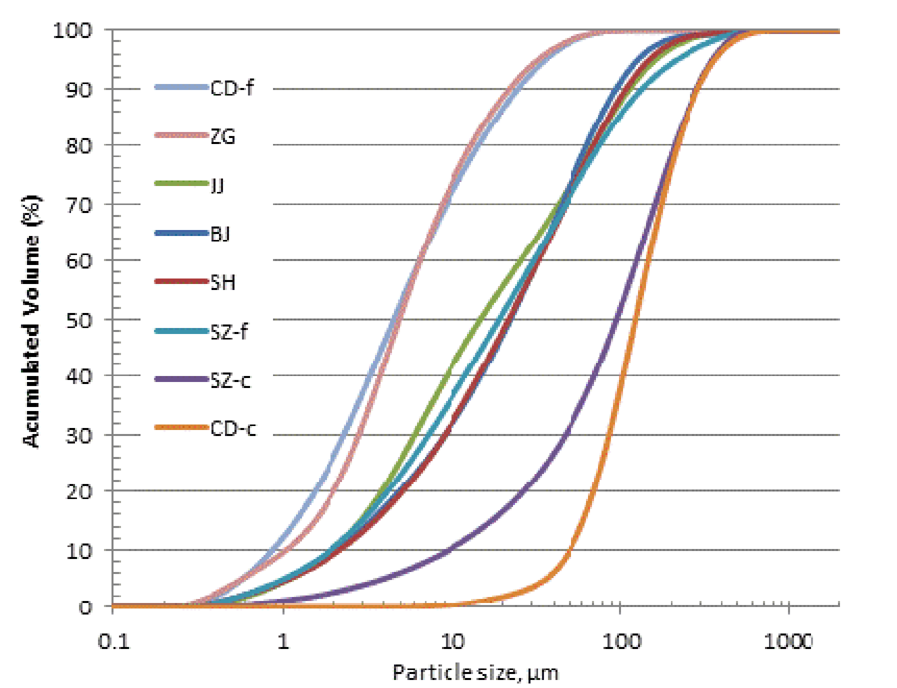

Figure 8 Accumulated particle size volumes of 8 fly ash samples

Table 4 Particle size rang, D_{50}, D_{90}, and wt% > 45 um of 8 fly ash samples

Sources	Range (μm)	D_{50} (μm)	D_{90} (μm)	wt%> 45 μm	GB1596-2005 Class
CD-f	0.2 -120	4.5	26	3%	I
ZG	0.2 - 140	5	23	2%	I
JJ	0.2 - 650	15	112	21%	II
BJ	0.2 - 725	22	97	16%	II
SH	0.2 - 650	22	112	21%	II
SZ-f	0.2 - 650	19	295	19%	II
SZ-c	0.2 - 725	95	138	61%	NR
CD-c	5.0 - 850	123	295	> 90%	NR

Figure 9 shows fine and coarse fly ashes from SZ and CD power plants. Obviously, CD is more efficient to produce finer fly ash and also coarse fly ash much coarser than SZ.

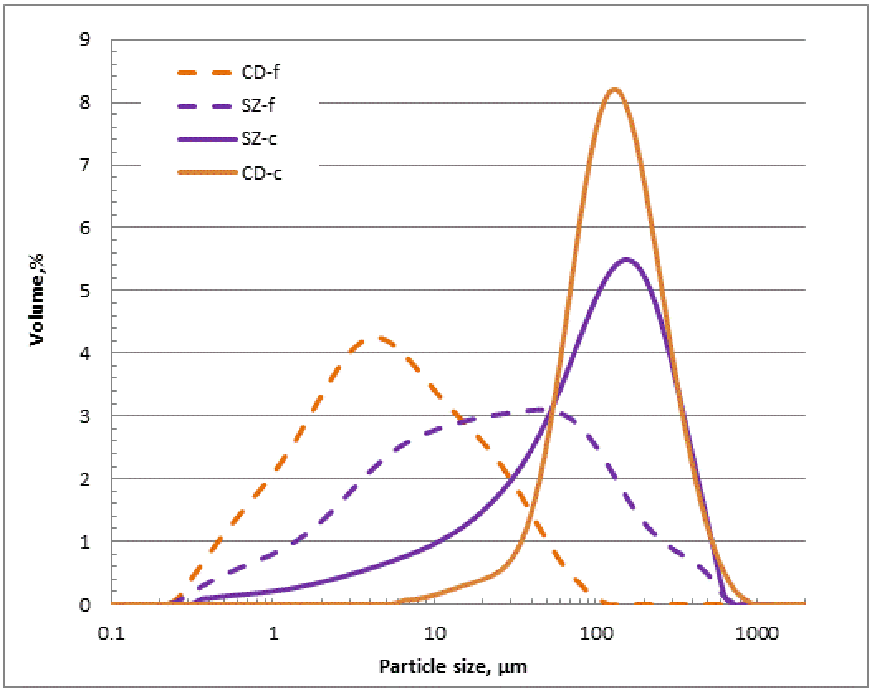

Figure 9 Particle size distributions of separated fly ashes from the same plant

The conventional wisdom states that finer fly ash can be collected by further electrostatic precipitator. Figure 10 shows 5 fly ashes collected from each precipitator at the same power plant, identified as SH-1, SH-2, SH-3, SH-4, SH-5, and their mixture as SH. Indeed, finer fly ash can be collected from the farther precipitator, but still has a very wide range of particle size distributions. However, the mixture is coarser than all fly ashes combined, and is believed due to mixing with bottom ash.

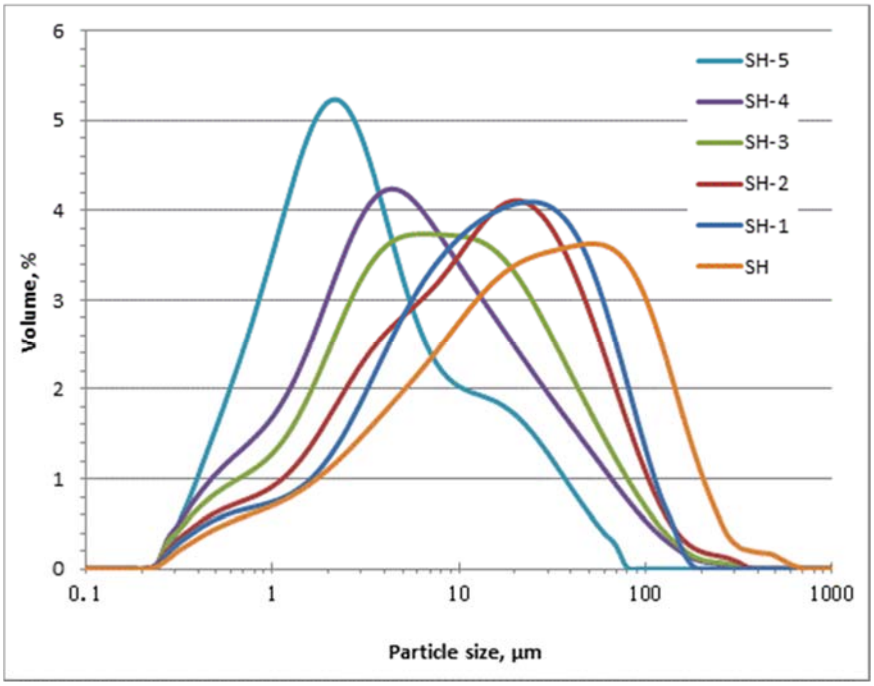

Figure 10 Particle size distributions for fly ashes from different precipitators

Figure 11 is the accumulated volume distributions of these fly ashes collected at different precipitators and their mixture. Table 5 lists the particle size range, D_{50}, D_{90}, and wt% > 45 μm of these fly ashes.

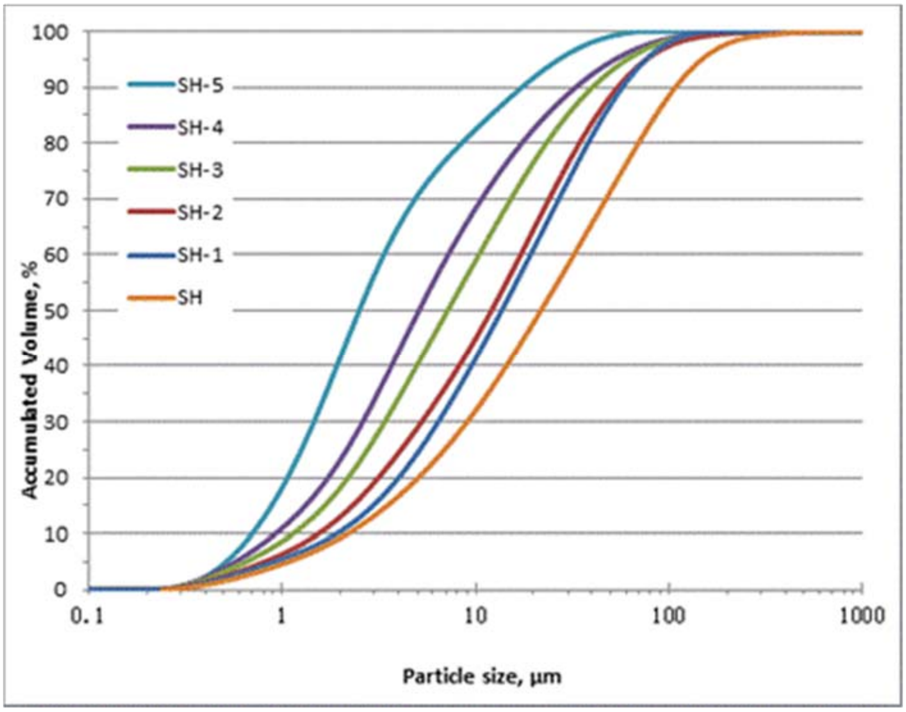

Figure 11 Accumulated particle size distributions of fly ashes from different precipitators

Table 5 Particle size rang, D_{50}, D_{90}, and wt% > 45 um of SH fly ash samples

Sources	Range (μm)	D_{50} (μm)	D_{90} (μm)	wt%> 45 μm	GB1596-2005
SH	0.2-650	22	112	21%	II
SH-1	0.2 -185	14	60	16%	II
SH-2	0.2 - 400	12	55	14%	II
SH-3	0.2 - 400	7	40	9%	I
SH-4	0.2 - 400	5	32	7%	I
SH-5	0.2 – 90	2.5	17	2%	I

In general, smaller particle size, larger surface area, higher reactivity, and higher value. Fly ash from different electrostatic precipitators should not be mixed together. Particularly, fly ashes from the last 3 precipitators meet Class I fineness requirements and should be collected separately. Even though the distribution ranges of these fine fly ashes are still wide, they should be more valuable for high value applications.

For chemical compositions, Table 6 lists 2 main and 4 minor compositions, their % and the ranges of these 6 fly ashes. Fly ash with Al_2O_3 > 35% is typically called as high Al fly ash, while < 20% as low Al fly ash. Fly ash is also classified into Class C or F based on its CaO content. Class C fly ash has the CaO content > 10% CaO in China, and can have cementitious reactivity when mixed with water, while Class F fly ash has the CaO content ≤ 10%. All fly ashes have pozzolanic reactivity.

Table 6 Main chemical compositions of 6 fly ashes

Compositions	BJ	SH	CD	SZ	JJ	ZG	Range
SiO_2	41.2	45.1	50.1	50.5	53.3	33.9	33-54
Al_2O_3	35.6	30.0	28.3	27.6	18.1	55.7	18 – 56
CaO	10.1	10.5	7.9	7.7	12.9	1.0	1 - 13
Fe_2O_3	5.9	6.5	5.6	7.0	5.5	2.2	2 – 7
SO_3	1.7	1.1	1.0	0.9	1.0	1.6	0.9 – 1.7
LOI	1.8	3.1	0.4	2.0	0.7	0.8	0.4 – 3.1
Other oxides	3.7	3.7	6.7	4.3	8.5	4.8	
f-CaO	0.6	0.9	0.5	0.8	1.5	0.3	0.3 – 1.5
SiO_2/Al_2O_3	1.2	1.5	1.8	1.8	3.1	0.6	0.6 – 3.1

Apparently, we can classify these 6 fly ashes into 3 groups based on their chemical compositions: ZG is a high Al but low CaO fly ash, JJ is high CaO but low Al fly ash, and the rest have typical Al and CaO values. Of course, there are other 3 groups; such as low or high CaO with typical Al, or high Al with typical CaO. However, fly ash with high Al does not mean that it will have higher Al in glass phase than fly ash with low Al.

The mineral compositions of these 6 fly ashes are listed in Table 7. The glass content range is from 42 to 68%. Glass content is the reactive phase containing aluminosilicates, while crystal phase consisting of many crystal minerals are quite stable. These 6 fly ashes can be classified into 3 groups. ZG with lowest glass content (42%) has the highest mullite content (51.1%) and corundum (6.4%) without any quartz. For the rest with glass content (52 – 68%) higher than crystal content, JJ has lowest mullite content (7.5%) but highest quartz (21.8%). The other four have typical values of 20 – 32% mullite, 8 – 10% quartz, Ca-containing minerals ≤6% and Fe-containing minerals ≤3%.

Table 7 Mineral compositions of 6 fly ashes

Source	Glass content	Mullite	Quartz	Corundum	Lime	Anhydrite	Gehlenite	Anorthite	Hematite	Magnetite
BJ	52.0	31.7	7.8	—	2.2	1.8	1.6	0.3	2.4	0.2
SH	52.9	29.9	10.2	—	1.2	1.8	—	1.7	2.1	0.2
CD	68.5	19.7	7.5	—	1.5	1.2	—	—	1.6	—
SZ	63.8	22.0	10.4	—	1.0	1.2	—	0.4	—	1.2
JJ	58.2	7.5	21.8	—	9.0	1.0	—	0.8	—	1.7
ZG	42.0	51.1	—	6.4	—	—	—	0.5	—	—

Among these 3 fundamental properties, particle size distribution has the widest variations, but it can be controlled to obtain the desired fineness or surface area, while chemical compositions, except LOI, and mineral compositions are given due to the fixed coal-fired power plant process and coal type used. Therefore, firstly select the right fly ash with suitable chemical compositions and mineral compositions suitable for the desired applications, and then control the particle size distribution so that fly ash with consistent quality can be obtained for further technology and product development.

MATERIALS SCIENCE BASED FLY ASH UTILZIATION AND CORE TECHNOLOGY DEVELOPMENT

From materials science standpoints, 3 fundamental properties of fly ash affect its end-use properties critical to its applications. Significant variations in these fundamental properties have been recognized as critical issues for fly ash to have consistent quality raw materials for various applications, particularly high value applications.[3] These 3 fundamental properties of fly ash are similar to 3 fundamental properties of polyolefin: particle size and its distribution ~ molecular weight and its distribution, chemical compositions ~ chemical structures (such as co-monomer type and amount), and mineral compositions ~ crystallinity (density). Figure 12 shows their similarities and differences between polyolefin produced from oil and fly ash generated from coal.

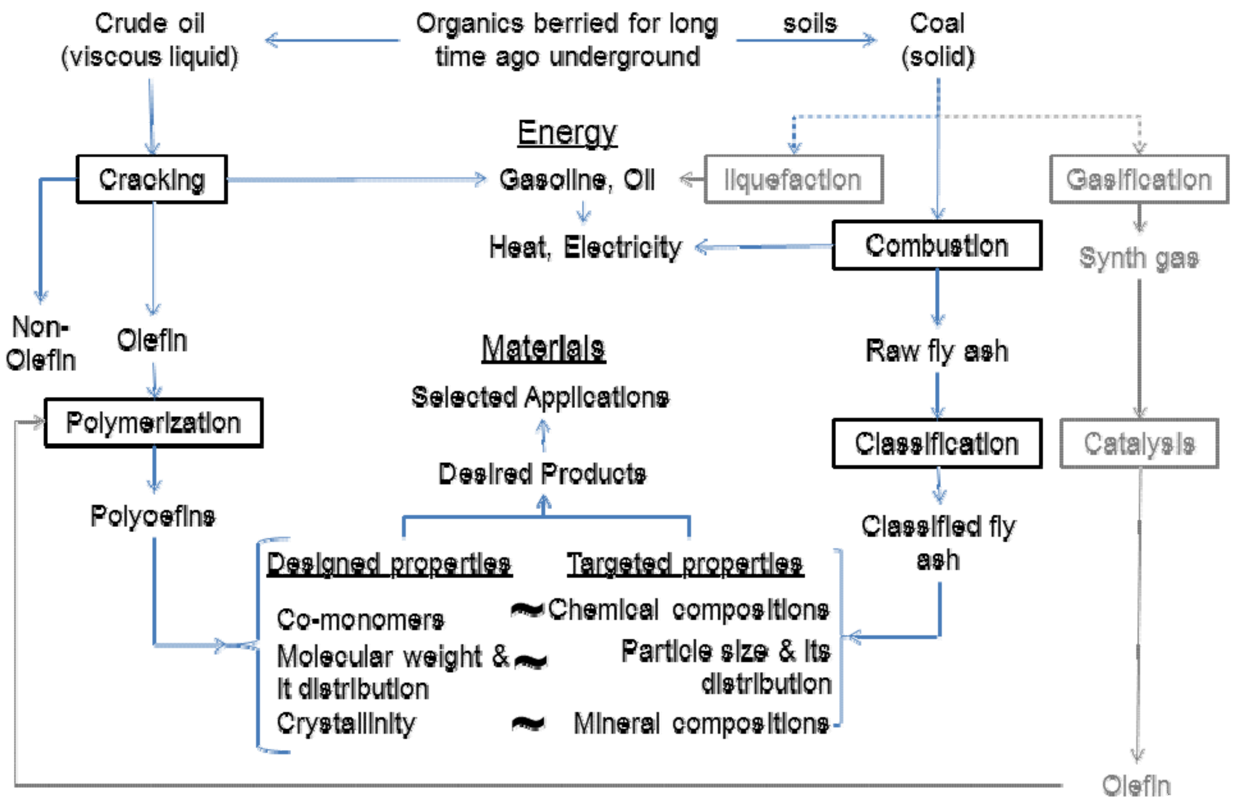

Figure 12 Similarities between polyolefin from oil and fly ash from coal for utilization

Obviously, each polyoefin is made with specific co-monomer type and level (crystallinity), molecular weight and its distribution for the desired applications. If various polyolefins with a wide range of molecular weights (such as 1 MI, 10 MI, and 100 MI) and distributions (such as1 MFR, 10 MFR, 100 MFR) are mixed, the mixture will be hard for any use and will be considered as a waste. Therefore, when we look at each fly ash produced from each coal-fired power plant, fly ash has unique chemical and mineral compositions but a broad range of particle size distribution. Instead of directly using for the low-end applications, each fly ash should be treated as a mixture of good quality classified fly ashes with different particle size distributions which can be separated into different fly ash classes with consistent quality in particle size distribution for suitable value-added applications.

We have measured fundamental properties of each fly ash produced from each coal fired power plant, and developed the comprehensive separation process to “transform” fly ash into different fly ash classes with desired particle size and distributions for further technology and product development for selected applications. We can also extract carbon from fly ash with higher LOI (> 5).

Through this materials science approach and simple classification process, we have developed 3 fly ash-based core technologies: high fly ash loading technology, geopolymer and its foam technology, and flame retardant and fillers technology as shown in Figure 13. Low carbon ready mix mortars and activated fly ash to replace cement were developed from our high fly ash-loading technology. Fire protection thermal insulation foam panels were developed from our geopolymer foam technology. Fly ash-based flame retardants for PP and PU and fillers for polymers and coatings were developed from our flame retardant and filler technology.

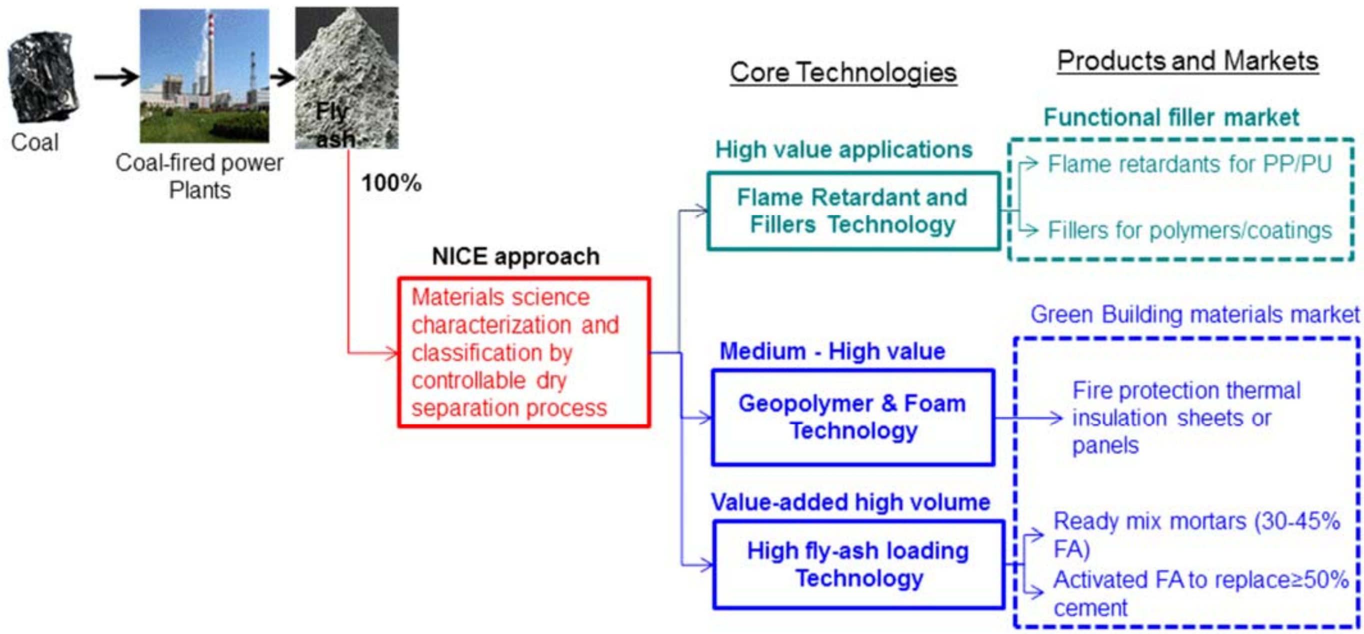

Figure 13.Core technologies developed at NICE and their products and applications

The first three products listed in Table 8 are green building materials for the building materials market, and the last 2 products are functional fillers for the fillers market.

Table 8 Core technologies, products, competitive products and markets

Core technologies	FA-based products	Existing products	Markets
High fly ash loading	Activated fly ash	Cement	Green Building Materials
	Low carbon mortar	Ready mix mortar	
Geopolymer & foam	Foam panel	Cement foam	
Fillers & Additives	Fillers	Inorganic fillers, $CaCO_3$,	Green Fillers
	Flame retardants	Phosphate-based flame retardant	

Activated fly ash can replace at least 50% cement used in commercial concrete, while low carbon ready mix mortar has at least 30% fly ash and can use up to 45% by weight. Fire protection thermal insulating foam panel from geopolymer foam technology can be used for external wall insulation to replace inorganic insulating materials including cement foam. Several fillers are developed to fully replace $CaCO_3$, partially replace carbon blacks, such as N990 or N774 in rubber applications. Two fly ash-based flame retardants were developed to replace two existing phosphate-based flame retardants, APP (Ammonium Polyphosphate) used for polyolefins and rubbers and DMMP (Dimethyl Methanephosphonate) used for PU foam.

NEW FLY ASH-BASED PRODUCTS AND THEIR POTENTIAL MARKET VALUES

Five types of new fly ash-based products from our 3 core technologies are listed in Table 8. All products consume at least 30% classified fly ash by weight considered as green products. However, the inherent issue is its grey color which may limit its certain applications. Below is market analysis for these new products and potential market values in China.

Green Building Materials

Building and construction is the major application for fly ash utilization. For example in 2011, China had 150 million tons fly ash consumed in 2,090 million tons cement, 71 million tons fly ash used in 740 million cubic meters concrete (1776 million tons), and 96 million tons fly ash used in bricks and walls. Bricks and walls included autoclaved aerated concrete blocks using fly ash up to 82% per GB/T 11968-2006, light building walls using fly ash up to 45% fly ash and 32% bottom ash per JG/T169-2005, and sintered porous bricks using fly ash up to 75% fly ash per GB 13544-2000.

Below are the potential market values from our activated fly ash to replace cement, low carbon specialty ready-mix mortar, and geopolymer foam for thermal insulation panels used in building and construction applications.

Activated fly ash

Fly ash, preferably with Al$\geqslant$28%, K$\leqslant$1.2%, $Ca^{+}\leqslant$1%, regardless of dry or wet, can be used as raw material to replace clay or bauxite to supply Al during sintering for making cement (~ 2 – 3% of the total weight). This does not need any fineness requirement. Fly ash has also been used as a supplemental cementitious material to partially replace cement in cement pastes or concretes for many decades. But it must meet the requirements according to GB/T 1596-2005 “fly ash technical requirements used for cement and concrete” as listed in Table 3. Not every fly ash produced from each coal-fired power plant can meet these requirements. However, fly ash used as an active cement mix in this standard does not have particle size but same chemical composition requirements, and can be used in 3 cement types, Ordinary, Fly ash and Composite Portland cements, according to GB 175-2007 in Table 9. The qualified fly ash can be used at the loading level of > 5% but ≤20%, >20% but ≤ 40%, or .20% but < 50% by weight in Ordinary, Fly ash or Composite Portland cements, respectively.

Table 9 GB175-2007 Common Portland Cements

Cement types	Class	Clinker + Gypsum	Granulated blast furnace slag	Pozzolana	fly ash	limestone
Portland	P·I	100%				
	P·II	≥ 95%	≤5%			
		≥ 95%				≤ 5%
Ordinary	P·O	≥ 80% < 95%	> 5% ≤20%			
Balstfurnace-slag	P·S·A	≥ 50% < 80%	> 20% ≤50%			
	P·S·B	≥ 30% < 50%	> 50% ≤70%			
Pozzolana	P·P	≥ 60% < 80%		> 20% ≤ 40%		
Fly ash	P·F	≥ 60% < 80%			> 20% ≤ 40%	
Composite*	P·C	≥ 50% < 80%	> 20% ≤50%			

'*At least 2 out of 4 active ingredients used, GBFS, Pozzolana, fly ash or limestone

Fly ash qualified according to GB/T 1596-2005 as Class I, II, or III fly ash can be used at its maximum loadings for different types of concrete depending on the cement type regulated by GB/J 146-1990 "technical guidance for fly ash used in concrete applications" as listed in Table 10. Qualified fly ash can be used as low as 10% for pre-stress steel concrete using blast-furnace slag Portland cement or as high as 65% for roller compact concrete using Portland cement.

Table 10 GB/J 146-1990 technical guidance for fly ash used in concrete applications

GB/J 146-1990	Maximum usage of fly ash			
Concrete type/Cement type	Portland	Ordinary	Blast-furnace slag	Pozzolana
Pre-stress steel concrete	25%	15%	10%	N/A
Steel concrete, High strength concrete, Anti-freeze concrete, Set concrete	30%	25%	20%	15%
Moderate or low strength concrete, Pumping concrete, Large volume concrete, Underwater concrete, Underground concrete, Pressure paste concrete	50%	40%	30%	20%
Roller compacted concrete	65%	55%	45%	35%

Currently, commercial concrete (typically pre-stress steel or steel concretes) has density about 2400 kg/m^3 and cement about 16% of its total composition where 4% (or 25% of the total cement) has been replaced with fly ash. Activated fly ash developed from our high fly ash loading technology can increase 25% to at least 50% cement replacement. Figure 14 compares 3-day and 28-day compressive strengths of our activated fly ash used in 50% cement replacement with Class II fly ash used in 0%, 25%, 30, and 50% cement replacement in the mortar formulations. The results clearly demonstrate that our activated fly ash can replace 50% cement to have 3-day and 28-day strengths higher than the existing one with 25% fly ash and as good as the sample without fly ash. This suggests that we can further increase the loading level of activated fly ash to the point where its compressive strength is equal to that with 25% Class II fly ash. This means more than 71 million tons fly ash to replace more than 50% cement used in concrete.

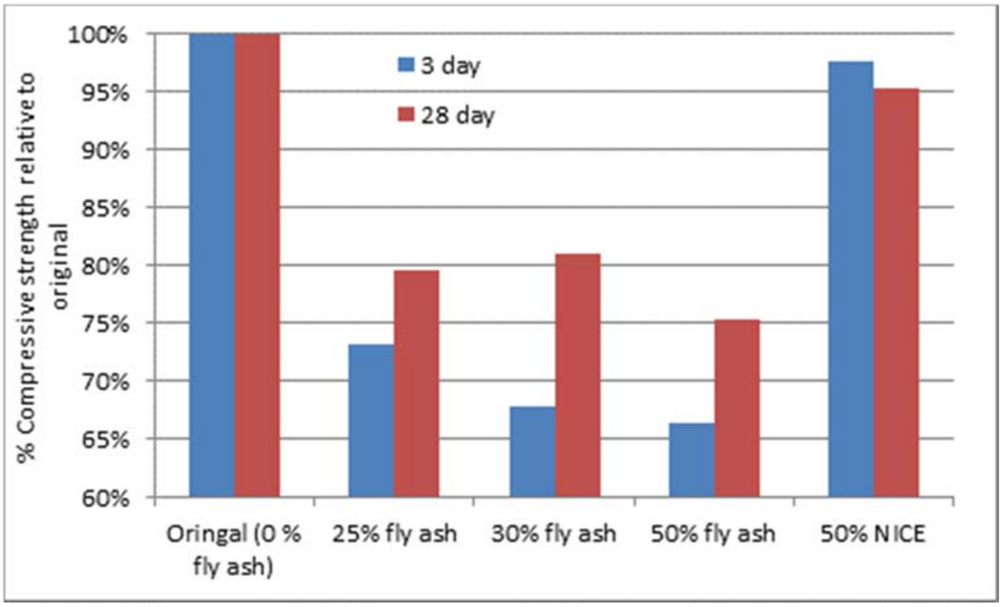

Figure 14 Compressive strengths of cement pastes w/wo fly ash or activated fly ash

Cement production typically produces 0.8 ton CO_2/ton cement. It also means replacing additional 71 million tons cement eliminates 56.8 million tons CO_2 emission due to our activated fly ash product. If this activated fly ash can be sold at ¥ 320/ton (cheaper than the cement price, typical ¥400/ton), the potential market value is ¥22.72 billion.

Low carbon ready-mix mortar

Mortar is one of large volume opportunities, after cements and concretes, for fly ash. The total mortar market size in China was reported about 1 billion tons in 2007. Mortar has two types: onsite and ready-mix mortar. Ready-mix mortar has been grown significantly in recent years due to environmental concerns and stringent air pollution regulations in big cities. The ready-mix mortar market size was about 11 million tons in

2007 with 60 – 70% AGR in the last 5 years. Ready-mix mortar also has two grades: general and specialty grade with the respective price range of ¥400 – 600/ton and ¥800 – 1,400/ton, much more expensive than on-site mortar in the price of ¥200 – 300/ton. Cost of ready mix mortar relative to on-site mortar is the barrier to its growth. Ready-mix mortar is expected to grow up to 100 million tons at least with about 75% general grade and 25% specialty grade in China in 2020. The specialty grade will have about 25 million tons with AGR more than 20% with 3 major types including tile adhesive mortar (50%), self-leveling mortar (15%), and thermal insulation adhesive and surface mortar (25%). The expected market size for thermal insulation adhesive and surface ready-mix mortars is about 6.25 million tons at the average price of ¥1,000/ton with the market value of ¥6.25 billion.

Due to inconsistent quality of fly ash from various sources, fly ash is rarely used in ready-mix mortar, particularly specialty grades. Our low carbon ready-mix adhesive mortar developed from our high fly ash loading technology contains 45% fly ash by weight and meets the requirements of JG/T 149-2003 standard for "expanded polystyrene board thin plaster exterior insulation system" as listed in Table 11. This low carbon ready-mix adhesive mortar is expected to have better flow properties as well as lower cost with no added value tax due to at least 30% fly ash by weight used in the total mortar formulation.

Table 11. Requirements versus performance of Low carbon ready-mix adhesive mortar

Adhesive strength (MPa)		Min. Requirements	Low carbon mortar
With cement paste block	14d	0.60	0.74±0.06
	14d + 7 d after water immersion	0.40	0.66±0.03
With expanded PS board and broken at its interface	14d	0.10	0.12±0.02
	14d + 7d after water immersion	0.10	0.10±0.01
Operating window (hours)		1.5-4.0	2.5

Fly ash-based geopolymer foam panel for thermal insulation

The comparison of various organic and inorganic thermal insulation materials is listed in Table 12. Organic insulation materials have dominated this market due to its excellent thermal insulation property, but have limited applications due to its poor fire rating. For external wall insulation, the fire rating requirement depends on the building height, such as h > 22 m for an A rating, 22 m ≥h > 7 m for a B1 rating, and h ≤7 m for a B2 rating according to GB 8624-2006. A new regulation for an A fire rating for all external wall insulation panels published on March 14, 2011. This triggered innovation in new inorganic material foam for better fire safety, such as cement foam with 200 – 300 kg/m^3, 0.058-0.065 W/mK, and 0.4- 0.5 MPa compressive strength.

Table 12. Comparison of various thermal insulation materials

<table>
<tr><th>Various insulation materials</th><th>Material</th><th>K (W/m.K)</th><th>Denisty (kg/m^3)</th><th>Compressive strenght (MPa)</th><th>FR ranking</th><th>Advantages</th><th>Concerns</th></tr>
<tr><td rowspan="5">Organic foam</td><td>EPS</td><td>≤ 0.03</td><td>≥ 32</td><td>-</td><td rowspan="3">B2</td><td rowspan="3">lower density and K, lower water absorption, low production cost</td><td rowspan="3">poor flame resistance</td></tr>
<tr><td>XPS</td><td>≤ 0.041</td><td>15-30</td><td>0.2-0.25</td></tr>
<tr><td>PU</td><td>≤ 0.025</td><td>≥ 35</td><td>≥ 0.1</td></tr>
<tr><td>Phenolic Resin</td><td>0.035</td><td>≤ 55</td><td>≥ 0.1</td><td rowspan="2">B1</td><td rowspan="2">Better FR, low water absorption</td><td rowspan="2">High price</td></tr>
<tr><td>Polyimide（PI）</td><td>≤ 0.035</td><td>≤ 55</td><td>≥ 0.1</td></tr>
<tr><td rowspan="6">Inorganic foam</td><td>Rock wool</td><td>0.04</td><td>-</td><td>-</td><td rowspan="6">A</td><td rowspan="6">High FR</td><td rowspan="2">high water absorption, shorter life</td></tr>
<tr><td>Glass wool</td><td></td><td></td><td></td></tr>
<tr><td>Glass foam</td><td>≤0.066</td><td>≥ 150</td><td>≥ 0.4</td><td rowspan="3">high energy process</td></tr>
<tr><td>Ceramic foam</td><td>0.03</td><td>-</td><td>-</td></tr>
<tr><td>Perlite</td><td>0.048</td><td></td><td></td></tr>
<tr><td>Cement foam</td><td>0.045</td><td>150-250</td><td>≥ 0.25</td><td>High water absorption, low strength</td></tr>
<tr><td rowspan="2">Organic/inorganic composite</td><td colspan="2">Layer structure</td><td></td><td></td><td rowspan="2">A or B1</td><td rowspan="2">High to better FR</td><td rowspan="2"></td></tr>
<tr><td colspan="2">Composite</td><td></td><td></td></tr>
</table>

The accumulated building area in China has reached 25 billion m^2. It was estimated about 95% required energy improvement. Assuming 5% improved annually, it has about 1.2 billion m^2 opportunity. In addition, the annual new building area is about 3 billion m^2. The total annual building area for energy improvement is about 4.2 billion m^2. Based on 0.6 for the insulation area to the total building area, the annual thermal insulation material is about 2.5 billion m^2. Based on the average thickness of 4 cm (3 cm thickness for southern regions but 6 cm thickness for northern regions), the insulation material volume is about 100 million m^3. Assuming the average density of thermal insulation material about 100 kg/m^3 (50 kg/m^3 for organic and 250 kg/m^3 for inorganic materials), the estimated market size is about 10 million tons (100 million m^3).

The price was ¥21/m^2 for EPS, ¥ 31.5/m^2 for XPS, ¥62.4/m^2 for PU, and ¥42/m^2 for rock wool in 2011. The price of cement foam was ¥72/m^2 in 2011 (at 6 cm thick) and down to ¥30/m^2 in 2014. The market trend indicates that the preferably price is not higher than

¥900/m^3 for new organic insulation materials and ¥500/m^3 for inorganic insulation materials. The inorganic insulation material market size is expected to have 5 million tons. The volume will be around 20 million m^3 at an average density of 250 kg/m^3. The market value is about ¥10 billion at the price of ¥500/m^3 (¥15 or 30/m^2 at 3 or 6 cm).

Our fly ash-based foam panel developed from our geopolymer & foam technology meets the Type II requirements according to JC/T 2200-2013 Foam product property requirements as listed in Table 13. Fly ash-based geopolymoer foam as a green material is also expected to absorb less water and have much stronger than other inorganic material-based foam.

Table 13. JC/T 2200-2013 Property requirements vs. geo-foams

Properties/Classification	Requirements		Geo-foam
	Type I	Type II	
Dry Density (kg/m^3)	≤180	≤250	201
Compressive Strength (MPa)	≥0.30	≥0.40	1.27
Thermal conductivity @25±2℃ (W/m.K)	≤0.055	≤0.065	0.057
Water absorption (% volume)	≤10		7.48
Dry shrinkage（after 24 hrs in water）mm/m	≤3.5		1.68
Vertical tensile strength (kPa)	≥80	≥100	
Combustion rating class	A_1		
Softening coefficient	≥0.70		
Carbonization coefficient	≥0.70		
Radiation: Internal and external indices	≤1.0		

Fly ash-based fillers

The global filler market size was estimated to be 125 million tons in 2010, including 71.7 million tons calcium carbonate $CaCO_3$ (57%), 27.4 million tons Kaolin (22%), 9.7 million tons Barytes (8%), 9.6 million tons arbon black (8%), and 7.6 million tons Talc (5%), and expected to achieve 150 million tons in 2015. Since fly ash has the inherent color issue, the estimated addressable filler market size in China for non-color sensitive filler applications is about 3 million tons in 2020 at the average price of ¥500/ton for polymeric and coating applications. The addressable filler market value in China for fly ash is estimated to be about ¥1.5 billion.

Fly ash as a green filler can improve processability, impact, scratch resistance due to its micro-nano spheres, and can resist high temperature and reduce shrinkage due to its high temperature incompressible nature. Table 14 compares test results of rubber formulations filled with fly ash filler, $CaCO_3$ and N-990.The results show fly ash filler can replace $CaCO_3$ or N-990 in this rubber formulation.

Table 14 Test results for rubber filled with fly ash filler, $CaCO_3$, and N990

Formulations	**A**	**B**	**C**
EPDM	115	115	115
$CaCO_3$	30		
Fly ash filler (NF008)		30	
N-990			30
N-650	98	98	98
Other additives	100.7	100.7	100.7
Total	343.7	343.7	343.7
Mooney ML 1+ 4 @ 100° C, MU	42	41	44
Mooney Scorch, MS @ 125°C			
t5/t35, sec	5.49/6.88	5.19/6.5	5.45/6.9
t35-t5, sec	1.39	1.31	1.45
Min Vis @ 125°C, MU	16.7	16.8	16.2
Rheometer at 177ºC			
ML/MH, dN-m	1.58/18.6	1.58/18.6	1.7/17.6
ts2, minutes	0.42	0.39	0.39
t'c90, minutes	3.06	3.43	2.56
Green properties			
25%/50% Modulus, MPa	0.249/0.309	0.231/0.287	0.242/0.303
Peak Tensile Strength, MPa	0.3	0.3	0.3
Elongation at Break, %	77	80	75
Cured Molded Slab Properties			
Hardness, Shore A	53	52	54
100%/300% Modulus, MPa	2.0/6.6	2./7.42	2.2/7.9
Tensile Strength at Break, MPa	9.4	11.1	10.9
Elongation at Break, %	428	456	444
Tear Strength, Die C, kN/m	30	26	30
Aged Physical Properties	70 hrs Hot Air Oven 125° C		
Hardness, Shore A	60	59	61
100%/300% Modulus, MPa	3.1/9.8	3.3/10.2	3.7/9.1
Tensile Strength at Break, MPa	10.9	10.9	10.2
Elongation at Break, %	345	329	278
Tear Strength, Die C, kN/m	26	24	27
Compression Set %			
Cured Buttons 22 Hours @ 70°C	14	14	12
Cured Buttons 168 Hours @ 80°C	39	37	38

Fly ash-based flame retardants

According to 2010 Fredonia data presented at the 2012 China Flame Retardant Society annual meeting, the global volume was reported to be 1.64 million tons in 2009 and will reach 2.3 million tons in 2015. Flame retardants used in China was estimated to be 320,000 tons with 4% AGR in 2010, and expected to reach 400,000 tons in 2020. It is estimated about 160,000 tons for polyolefin and 80,000 tons for polyurethane (PU) foam.

Fly ash has been reported in literature to improve flame retardance in several polymers, such as polycarbonate, polyvinyl chloride, epoxy resins, epoxy and polypropylene blends, or rigid polyurethane foam (RPUF) synergistic with ammonium polyphosphate (APP) and pentaerythritol (PER). But so far, no fly ash-based flame retardant is available in the marketplace. Two fly ash-based flame retardants from our functional filler technology have been developed to replace APP priced at ¥20,000/ton for polyolefin and rubbers and to replace DMMP (Dimethyl methanephosphonate) priced at ¥30,000/ton for PU foam. The potential market value is about ¥3.2 billion to replace APP used for polyolefin and rubbers and about ¥2.4 billion to replace DMMP used for PU foam.

Table 15 is the example of our fly ash-based flame retardant, NFR35, compared with existing flame retardants, brominated flame retardant, phosphates, and $Mg(OH)_2$ in polyolefin blends. However, our fly ash-based flame retardants as green fillers have the grey color which may limit its market share but they can offer lower cost and better processability which is typically compromised by phosphates or metal hydrates.

Table 15 NFR 35 compared with brominated FR, Phosphate, and $Mg(OH)_2$ in polyolefin

Sample ID	PP	POE	FR level	LOI	UL-94			Tensile (MPa)	Elongation （%）
					t1 (s)	t2 (s)	Rank		
PP-POE with Br FR	63	21	16	24.4	0.6	0.8	V0	21.2	399.9
PP-POE Phosphate FR	53	18	29	22.1	18	30	V1	21.6	364.8
PP-POE with Mg(OH)2	34	11	55	23.5	0.7	0.8	V0	9.0	32.2
PP-POE with NFR 35	41	14	45	27.5	0.6	1.8	V0	19.3	387.4

CONCLUSION

China is a coal rich country, and coal is the primary nature resource to support its economic growth. The fly ash volume in China is expected to continuously grow but not expected to exceed 600 million tons in 2020 due to the maximum coal assumption of

4.2 billion tons set by the central government. The un-utilized fly ash volume has reached 170 million tons or more. How to increase fly ash utilization and its value to reach its full utilization for each coal fired power plant, regardless of the plant location, is the challenging and critical task in China.

The main issue is the concept and approach of fly ash utilization to deal with its massive volume and significant property variations: solid waste utilization vs. materials science based value creation. Solid waste utilization focuses on fast and massive utilization with high tolerance in property variation, resulting in massive local low-value utilization. Materials science based value creation needs to identify and create sufficient needs in local and beyond local markets and to generate sufficient utilization value so that the solutions can be implemented profitably by fully utilizing fundamental properties of fly ash through the most cost-effective core technologies and products.

This paper demonstrates that the scientists at NICE, a subsidiary of Shenhua Group as one of the world largest coal producers, for the last 3 years have developed 3 core technologies and 5 products for the selected markets to significantly increase fly ash utilization value based on materials science concept and approach. The estimated market opportunity in China is over ¥42 billion revenue and over 50 million tons CO_2 reduction with the maximum fly ash consumption to make these newly developed fly ash-based products over 70 million tons. However, this is still not big enough to cover the un-utilized fly ash volume over 170 million tons in China. Therefore, the scientific community needs to continue developing new products for new applications based on the existing core technologies, and developing new core technologies and products for new opportunities to create sufficient values, particularly for high value applications, based on materials science concept and approach.

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