Dry FGD By-Product Characteristics and Utilization - International Perspective

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ABSTRACT

Dry process is a major technology for flue gas desulfurization (FGD) other than wet process. It has advantages of lower capital cost and power usage, less land use, no waste water treatment and of application to the regions with limited water resources. In recent years, dry FGD process has been developed into a multi-pollutants (SO_3, HCl, HF and Hg) control technology. In addition, it becomes competitive for use in a large-scale power plant burning a high sulfur coal, due to the emerging more efficient dry FGD technologies such as circulating fluidized-bed flue gas desulfurization (CFB-FGD) and NID processes. However, the utilization of Dry FGD by-product has been developed slowly. In contrast to FGD gypsum, the major sulfur-containing component in dry FGD by-product generated from the desulfurization system is calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$). Compositions and properties of by-products are often site-specific and can be affected strongly by coal types, flue gas compositions, unit operating conditions and other factors.

In this paper, characteristics and utilization of dry FGD by-products from different sources in China and US will be compared. The recent development in by-product utilization, especially in China, will be discussed. In addition, an international cooperation program between research and industrial organizations in US and China to advance by-product utilization will be illustrated.

INTRODUCTION

Dry process is an alternative to wet process for flue gas desulfurization (FGD). In recent years, dry FGD process has been developed into a multi-pollutants (SO_3, HCl, HF and Hg) control technology and widely applied to coal-fired power plants, iron and steel sintering plants, circulating fluidized-bed (CFB) boilers as polishing units and industrial installations. In addition, it becomes competitive for use in a large-scale power plant burning a high sulfur coal, due to the emerging more efficient dry FGD technologies such as CFB-FGD and NID processes[1]. However, the utilization of dry FGD by-product has been developed slowly. Barriers to dry FGD by-product utilization are related mainly to lack of understanding of the materials and lack of systematic evaluation of relevant utilization issues[2,3]. In contrast to FGD gypsum, the major sulfur-containing component in dry FGD by-product is calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$). Characteristics (compositions and properties) of by-products are often site-specific and can be affected strongly by coal types, flue gas compositions, unit operating conditions and other factors. In spite of these, dry FGD by-products have been utilized in US, Europe and China. Utilization is related to dry FGD by-product characteristics and, as expected, affected by economics and legislation. These experiences can be used as guidelines or references to advance further development of dry FGD by-product utilization.

In this paper, characteristics of dry FGD by-products and the status of utilization in US, Europe and China will be compared, according to the scope of applications. The recent development in by-product utilization, especially in China, will be discussed. In addition, an international cooperation program between research and industrial organizations in US and China to advance standardized utilization of dry FGD by-product will be illustrated.

DISCUSSION

Characteristics of Dry FGD By-Products

Major dry FGD technologies include spray dryer absorber (SDA), CFB-FGD and NID processes. SDA process has been applied to coal-fired power plants, since 1970's. CFB-FGD and NID processes, often called CDS (circulating desulfurization scrubber) in US, have been emerging as new dry FGD technologies in 2000's, due to better calcium utilization efficiency (lower Ca/S ratio) for flue gas desulfurization and multi-pollutants (SO_3, HCl, HF and Hg) control capacity[4]. Compositions of by-products generated from these processes are similar. The main sulfur-containing component in dry FGD by-product is calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$). Other mineralogical compositions are similar except differences in distribution of components, which is often site-specific. Characteristics of dry FGD by-products are discussed below in accordance with dry FGD process applications in coal-fired power plants, iron and steel sintering plants and CFB boilers as polishing units.

Coal-Fired Power Plants

Dry FGD by-products generated from coal-fired power plants can have different fly ash contents. Fly ash contents are mainly affected by the particulate removal devise (i. e., baghouse or ESP) installed prior to the FGD unit for ash pre-collection. In US, there is generally no ash pre-collection devise installation[2,3]. Dry FGD by-products usually contain a substantial amount of fly ash components. In Europe, a particulate removal device with high efficiency is installed for ash pre-collection. Dry FGD by-product usually contains only a very small amount of fly ash components (< 10%)(2,3). In China, a particulate removal devise is often located prior to the FGD unit for ash pre-collection as in Europe. However, the amount of fly ash components in dry FGD by-product is dependent on efficiency of the particulate removal operation. As shown in Figure 1, major elemental compositions (Si, Al, Fe, Ca, S) of dry FGD by-products collected from five power plants with decreasing ash pre-collection efficiency from #1 to #5, are compared with those in fly ash (#6). The elemental compositions are reported in oxide forms. The total amount of SiO_2, Al_2O_3 and Fe_2O_3, as an indication of fly ash components, decreases with increasing amounts of CaO and SO_3 . Dry FGD by-products have elevated Ca and S contents in comparison to those in fly ash.

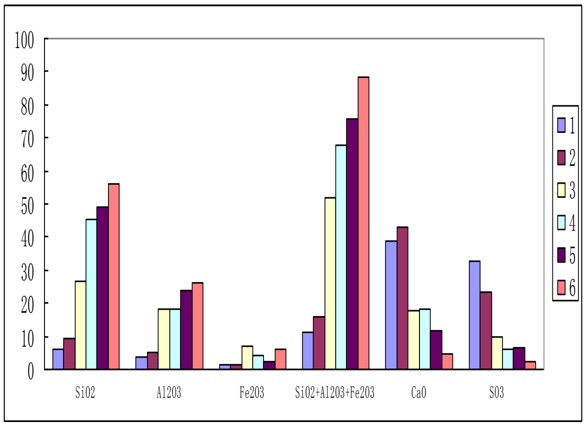

Figure 1 Elemental Compositions in Dry FGD By-products from Power Plants with Different Ash Pre-Collection Efficiency

Figure 2 shows particle size distributions of dry FGD by-products collected from five power plants with different fly ash contents in China. The D_{50} particle sizes are low than 30 μm, indicating that dry FGD by-product has a fine particle size distribution. D_{50} and D_{90} particle sizes increase with increasing amount of fly ash in these dry FGD by-products.

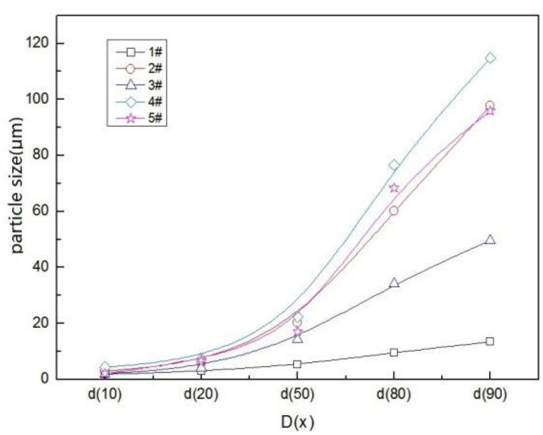

Figure 2 Particle Size Distributions of Dry FGD By-products from Power Plants with Different Fly Ash Contents

Major mineralogical components in dry FGD by-products are calcium sulfite hemi-hydrate ($CaSO_3 \cdot 1/2H_2O$) and calcium carbonate ($CaCO_3$). The minor mineralogical components are hydrated lime ($Ca(OH)_2$) and calcium dihydrate ($CaSO_4 \cdot 2H_2O$). The amount of fly ash mineralogical components (SiO_2 , $3Al_2O_3 \cdot 2SiO_2$) in dry FGD by-products is dependent on efficiency of ash pre-collection and can be a major or minor component..

The cementitious properties of dry FGD by-products generated from coal-fired power plants are related to fly ash and hydrated lime contents. In US, most of dry FGD by-products can be used directly for its inherent cementitous properties. In Europe, addition of fly ash is sometimes needed, if cementitious properties are required for utilization. In China, the cementitious properties of dry FGD by-products are varied and dependent on operating efficiency of the ash pre-collection unit.

Iron and Steel Sintering Plants

Dry FGD process has been widely used for flue gas clean up in China. Dry FGD by-product, generated from a Iron and steel sintering plant, has a low fly ash component, due to the high ash pre-collection efficiency to remove particulates from flue gas, probably with except of Fe_2O_3. As shown in Figure 3, major elemental compositions (Si, Al, Fe, Ca, S) collected from five iron and steel sintering plants are listed for comparison. The elemental compositions are reported in oxide forms. The SiO_2 and Al_2O_3 contents are low，indicating low fly ash content. Dry FGD by-products have higher elevated Ca and S contents than those in coal-fired power plants.

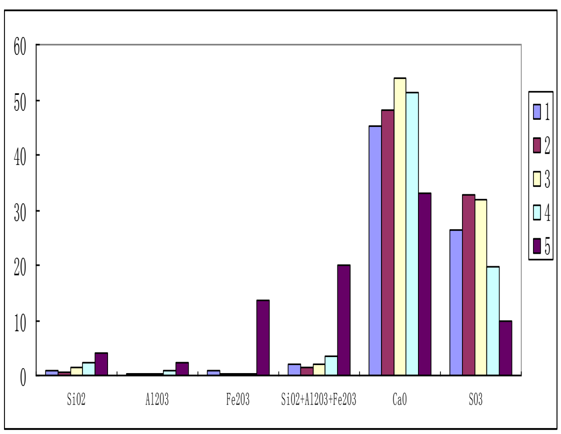

Figure 3 Elemental Compositions in Dry FGD By-products from Iron and Steel Sintering Plants

Figure 4 shows particle size distributions of dry FGD by-products collected from five iron and steel sintering plants. The D_{50} particle sizes are below 20 μm, which are finer than those in coal-fired power plants, probably due to lack of fly ash components.

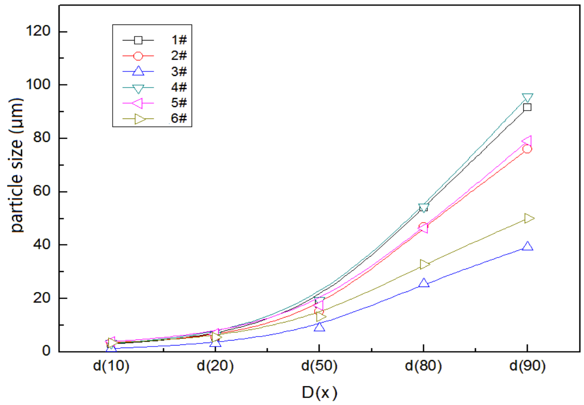

Figure 4   Particle Size Distributions of Dry FGD By-products from Iron and Steel Sintering Plants

The major mineralogical components in dry FGD by-products are calcium sulfite hemi-hydrate ($CaSO_3 \cdot 1/2H_2O$) and calcium carbonate ($CaCO_3$). The minor mineralogical components are hydrated lime ($Ca(OH)_2$), calcium dihydrate ($CaSO_4 \cdot 2H_2O$) and fly ash. By-Product can contain high $CaSO_3 \cdot 1/2H_2O$ content (up tp 60%) and $CaCO_3$ contents (up to 30%), due to the lack of the fly ash component.

Dry FGD by-products generated from iron and steel sintering plants usually have relatively low cementitious properties. Addition of pozzolans (e.g.,fly ash, slag) is generally required for utilization as fill materials with structural integrity. By-products containing high $CaSO_3 \cdot 1/2H_2O$ and $CaCO_3$ contents can benefits certain applications.

Polishing Unit of CFB Boiler

In circulating fluidized-bed (CFB) boiler, limestone ($CaCO_3$) is injected at 850 – 950° C to form lime (CaO) and reacts with sulfur dioxide in flue gas to form anhydrite ($CaSO_4$) for desulfurization. By-Products generated from CFB boilers are mainly composed of $CaSO_4$, un-reacted CaO and residual coal ash. The sulfur removal efficiency in CFB boiler is generally up to 80%. To meet stringent environmental regulations in US and China, dry FGD process has been used as a polishing unit to further reduce sulfur emissions from CFB boiler. Since most of sulfur is removed in the CFB boiler, major sulfur-containing component in dry FGD by-product is $CaSO_4$ with $CaSO_3 \cdot 1/2\ H_2O$ as a minor component, if there is no ash pre-collection unit between boiler and dry FGD system. As shown in Table 1, elemental compositions of three by-products are compared.   These data reflect the trend of elemental compositions in by-products generated from fuels with different ash and sulfur contents. The by-product generated from 70/30 petcoke/coal has the highest sulfur and calcium contents and the lowest ash content. The by-product generated from gob (or waste coal) has the lowest sulfur and calcium contents and the highest ash content with by-product generated from coal combustion in-between. These differences can have direct effect on by-product compositions and utilization.

Table 1 Major Elemental Compositions of By-Products from Three CFB Boilers with Dry FGD as Polishing Units

Major Element (a)	Weight Percent (wt%)		
SiO_2	15.15 (b)	38.90 (c)	47.71 (d)
Al_2O_3	9.40	13.31	28.25
TiO_2	0.40	0.50	1.01
Fe_2O_3	1.73	5.91	3.64
CaO	44.87	17.61	7.46
MgO	1.69	2.62	1.24
Na_2O	0.10	0.51	0.31
K_2O	0.49	0.83	1.84
P_2O_5	0.05	0.41	0.23
SO_3	21.78	7.53	4.03
SiO_2+Al_2O_3+Fe_2O_3	26.28	58.12	76.60

(a) Reported in oxide form
(b) Burning 70/30 petcoke/coal in China
(c) Burning low sulfur coal in US
(d) Burning gob with high ash and low sulfur

The major mineralogical components in dry FGD by-products generated without ash pre-collection units are anhydrite ($CaSO_4$), lime (CaO) and coal ash. The minor mineralogical components are hydrated lime ($Ca(OH)_2$), calcium sulfite hemi-hydrate ($CaSO_3 \cdot 1/2H_2O$) and calcium carbonate ($CaCO_3$). If there is an ash pre-collection unit between boiler and dry FGD unit, distribution of these mineralogical components could be different, depending on operating efficiency of ash pre-collection unit.

Dry FGD by-product, generated from CFB boiler with a polishing unit, generally has inherent cementitious properties, which are related to CaO and coal ash contents. However, sufficient hydration of CaO to $Ca(OH)_2$ is usually required to reduce expansive potential for utilization. By-product, generated from gob with low sulfur and high contents, has high potential for use in building materials.

Utilization of Dry FGD By-Products

Utilization of Dry FGD By-Products in US and Europe.

The utilization of dry FGD by-product is reported annually by the American Coal Ash Association (ACAA) in US and by the European Coal Combustion Product Association in Europe. In the ACAA report, it is referred as “FGD Material Dry Scrubber”. In the ECOBA report, it is reported as “SDA Product”, indicating most of dry FGD by-product is generated from SDA process in Europe.

Utilization of dry FGD by-product in US

According to the ACAA report, 2,180,474 tons of dry FGD by-product was produced in2011[5]. Of that, 571,381 tons (or 26.21%) was utilized. In comparison, 1,405,952 tons of dry FGD by-product was produced in 2010. Of that, 584,112 tons (or 41.50%) was utilized. Production of dry FGD by-product increased with decreasing utilization from 2010 to 2011. Figure 5 illustrates the major market for dry FGD by-product in US.

It is mostly utilized in soil modification/stabilization (38.27%), mining applications (26.09%), waste stabilization/solidification (15.47%) and structural fills/embankments (9.95%), which are related to cementitious properties of dry FGD by-products.

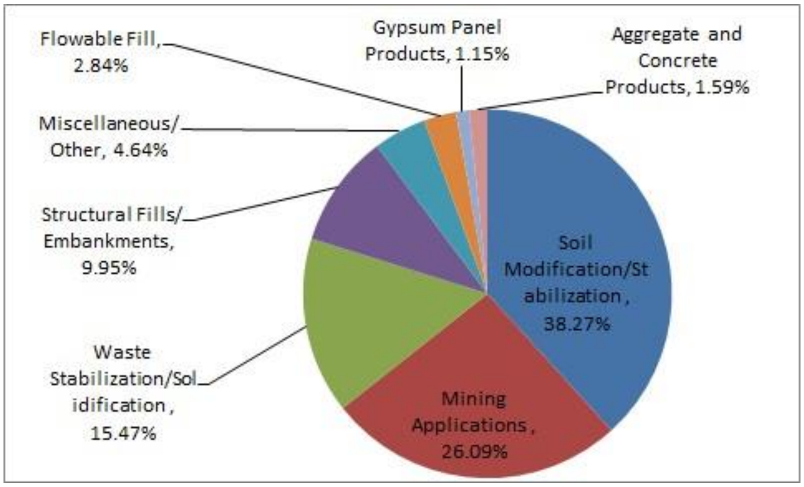

Figure 5 Major Markets of Dry FGD By-Product in the United States

Utilization of dry FGD by-product in Europe

According to the ECOBA report, 306,000 tons of dry FGD by-product was produced in 2009[6]. Of that, 270,000 tons (or 88.00%) was utilized. Figure 6 illustrates the major market for dry FGD by-product in Europe. It is mostly utilized in reclamation and restoration (33.7%), structural fill (25.6%) and infill applications (20.3%). In these applications, addition of fly ash is sometimes required to enhance cementitious properties

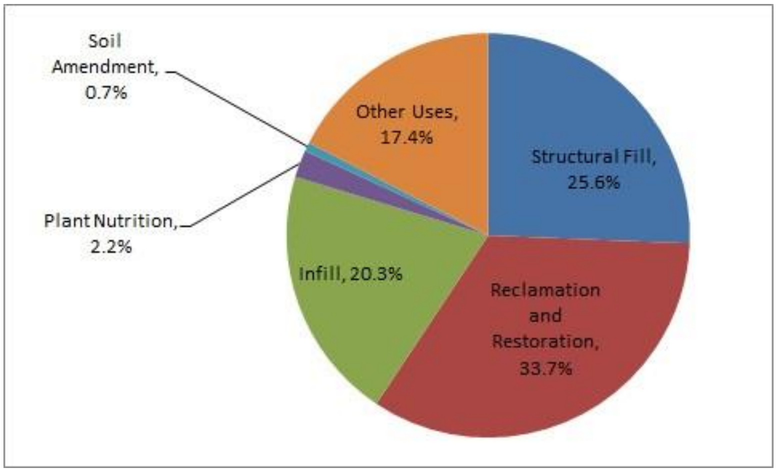

Figure 6 Major Markets of Dry FGD By-Product in Europe

Utilization of Dry FGD By-Products in China

Dry FGD process, especially CFB-FGD technology, has been widely applied to coal-fired power plants, iron and steel sintering plants, circulating fluidized-bed (CFB) boilers as polishing units and industrial installations since early 2000[7]. It is estimated that about four million tons of dry FGD by-product was produced in 2012. The quantity will increase substantially in the future. However, there is no official statistics of dry FGD by-product production and use available in China. The information of utilization discussed below is based on published literatures, reports, conferences and contacts with users of dry FGD process in China. The discussion is emphasized on recently developed applications using dry FGD by-products as building materials, which is different from current developments in US and Europe.

Autoclaved Brick

Autoclaved brick has been produced commercially with fly ash as a mix component in China since 2000. It is used to replace clay brick, which is currently banned for production in China. The major feed components for autoclaved brick production are fly ash, quick lime (or hydrated lime) and filling materials or aggregates such as sand, crushed stone, slag and others. The flow diagram for autoclaved brick production is shown in Figure 7. Dry FGD by-product with proper composition and mix design can be used as a feed component for autoclaved brick production[8]. Up to 20% dry FGD by-product addition has already been used commercially. Picture of a plant operation is shown in Figure 7. Pilot plant study is currently being conducted in a production line with dry FGD by-product addition up to 40%[8].

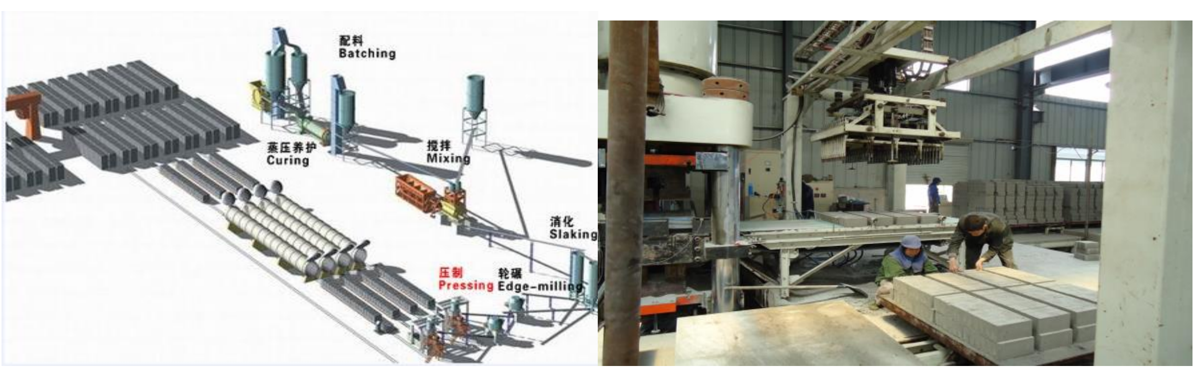

Figure 7 Flow Diagram (right) and Plant Operation (left) of Autoclaved Brick Production

Autoclaved Aerated Concrete

Autoclaved aerated concrete using fly ash as a feed component has been produced commercially as a lightweight concrete product for over forty years in China. The major feed components for autoclaved aerated concrete production are fly ash, lime, cement gypsum, aluminum powder and filling materials. The flow diagram for autoclaved aerated concrete production is shown in Figure 8. Dry FGD by-product with proper composition and mix design can be used as a feed component for autoclaved aerated concrete production[8]. Up to 10 % dry FGD by-product addition has already been used commercially for production in China. Picture of a plant operation is shown in Figure 8. Pilot plant study was conducted in a production line with dry FGD by-product addition up to 15%[8].

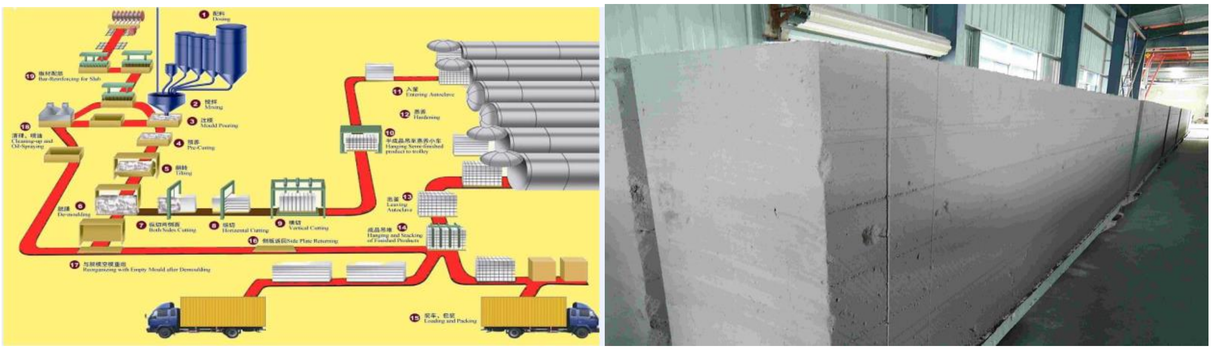

Figure 8 Flow Diagram (right) and Plant Operation (left) of Autoclaved Aerated Concrete

Ground Granulated Blast Furnace Slag (GGBS)

A dry FGD by-product with a fine particle size distribution and proper chemical compositions can be used as an admixture in production of GGBS. Addition of a small amount of dry-FGD by-product does not affect characteristics of GGBS (activity index, fluidity and others)[8]. Up to 5% dry FGD by-product addition has already been used commercially in China. Picture of an operation plant is shown in Figure 9. The amount of addition is restricted by sulfur chlorine and content of the dry FGD by-product.

Figure 9 Operation Pl ant of GGBS Production with Dry FGD By-Product Addition

Mortar

Addition of a dry FGD by-product with proper characteristics can have positive effects on mortar strength, water retention, density and others. Dry FGD by-product has been in commercial use to improve properties of mortar[8,9]. Its application is related to characteristics of the dry FGD by-product such as particle sizes, $CaCO_3$ and $CaSO_3 \cdot 1/2H_2O$ contents. The effect of dry FGD by-product addition on mortar properties and long-term stability are needed to be verified. Figure 10 shows a picture of mortar application with dry FGD by-product (bagged) addition.

Figure 10 Mortar Application with Dry FGD By-Product (bagged) Addition

Cement and Concern

Dry FGD by-product has been reported for use as a retarder to replace gypsum and a pozzolanic admixture to replace fly ash in cement and concrete in China. However, it is difficult to verify the progress. Based on studies by Lonjing Environment Technology Co. Ltd. (LETC)[8] and others[10, 11], its applicability is related to characteristics of dry FGD by-product and cement clinker. Specific evaluation is required to verify the feasibility. In addition, long-term stability could be a concern. A collaboration program by LETC has been established with domestic and international research institutes to advance cement and concrete applications.

Highway Construction

Dry FGD by-products have been used commercially in road base stabilization and as asphalt filler in surface course for road and highway construction[12]. Utilization in embankment construction has also been reported. The utilization is limited by seasonal and construction demands.

Mine Application

Dry FGD by-products with cementitious properties have been used as filling materials in mines, mostly in Northern and Western regions of China. The utilization is restricted by logistics issues and potential impact on environments.

Agricultural Application

Dry FGD by-product has been evaluated in a large scale as plant nutrient and agent to treat salty soil. Test results indicate that concentrations of the leachable toxic trace elements are well below the allowable limits[13]. Dry FGD by-product has also been processed by mixing with potassium feldster and heating for decomposition at 800 – 900 ˚ C , producing a fertilizer, which contains Ca, Si and S (from dry FGD by-product) potassium and magnesium (from potassium felstder)[14]. The modified dry FGD by-product fertilizer works well in green house experiment testing and rice field, as shown in Figure 11.

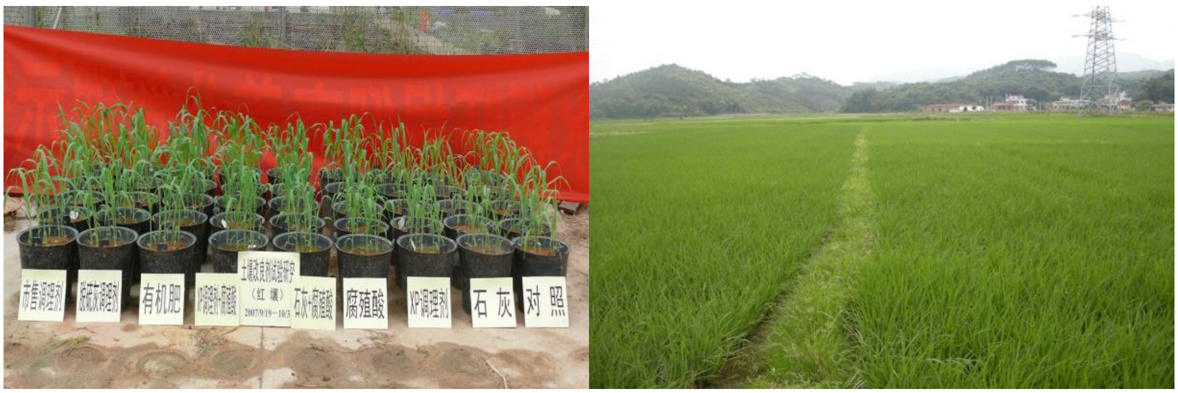

Figure 11 Application of Modified Dry FGD By-Product Fertilizer

As discussed above, it is feasible to use dry FGD by-products in building materials, highway construction, mine application, structural fill, agricultural application and others. Some of these, especially in new building materials, have already been utilized in China. However, dry FGD by-product is relatively new and only started to produce in early 2000 in China[7]. More systematic studies are needed to correlate characteristics of dry FGD by-product with standardized utilization. The current utilization experience can also be used as guidelines or references to advance further development of utilization.

INTERNATIONAL COLLABORATION

An international collaboration program has been developed among Lonjing Environment Technology Co. Ltd (LETC) in China, the University of Kentucky Center of Applied Energy Research (UK/CAER) and the Ohio State University School of Engineering (OSUSE) in US. The objective is to combine complimentary resources and experience of research and industrial organizations in US and China to overcome barriers and to advance dry FGD by-product utilization in both countries.

To address the needs for cement application and durability of building material products, the initial collaboration between LETC and UK/CAER is emphasized on the role of sulfite in dry FGD by-product on cement and concrete applications and on the long-term stability of building material products made with dry FGD by-product generated from different sources as feed components. To address the needs for standardized utilization of dry FGD by-product in construction and environmental concerns, the initial collaboration between LETC and OSUSE is emphasized on engineering applications such as soil stabilization and flowable fill with dry FGD by-product generated from different sources and on environmental issues such as the leaching behaviors of dry FGD by-products and their relationships with utilization. Further collaboration could be developed to facilitate standardized utilization of dry FGD by-product in different areas. .

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