Development of Key Technologies for Dry FGD By-Product Resource Comprehensive Utilization: A Project History

Qingfa Su[1], Tomas L. Robl[2], Robert B. Jewell[2], William E. Wolfe[3], Tarunjit S. Butalia[3], Zhongren Zhao[4], Maoyuan Lu[1], Yongrui Chen[1] and Muh-Cheng M. Wu[1]

[1] Lonjing Environment Technology Co. Ltd, Longking Square, No.399, Linhou Road, Xiamen, Fujian, China, 361009
[2] University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511
[3] Department of Civil, Environmental and Geodetic Engineering, The Ohio State University, Columbus, OH 43210
[4] PetroChina Jilin Petrochemical Company Second Power Plant, Jilin, China, 132000

KEYWORDS: Dry FGD By-Product, Utilization, International corporation

ABSTRACT

The project, entitled "Cooperative Development of Dry FGD Byproduct Resource Comprehensive Utilization key Technology And Core Equipment" (DFB93990), was carried out by Lonjing Environment Technology Co Ltd. (LETC) in China with collaboration of Green Byproduct Consulting Company LLC, Ohio State University College of Engineering (OSUCOE) and University of Kentucky Center of Applied Energy Research Center (UK/CAER) in the US during the period of 2010 - 2013. Funding of the project includes 2.97 million RMB from the Chinese Ministry of Science and Technology and 11 million RMB from LETC, a total of 13.97 million RMB. From the project, a Sino-American Flue Gas Cleaning Byproduct Resource Research Center was established.

Based on the US experience, it is to establish a platform specializing in characterization of dry FGD byproduct chemical and physical properties and the research center specializing in comprehensive utilization evaluation of dry FGD byproducts generated from various sources with different characteristics. The evaluation focuses on seven classes of building material applications in line with China's national conditions and needs, including autoclaved brick, autoclaved aerated concrete block, mortar, lightweight aggregate, ground granulated blast furnace slag (GGBS), laminate flooring and standardized cement application with significant results. A total of six national patents have been applied, five of them have been authorized.

Based on bench-scale evaluation, we constructed a 120 million autoclaved brick production line with annual consumption of over 100 thousand tons of dry FGD byproduct in Jilin Province, China, and completed autoclaved aerated concrete block, mortar and GGBS production lines for utilization demonstration and promotion with annual consumption of 80 thousand tons of dry FGD byproduct from an iron and steel plant in Nanjing, Jiangsu, China

During project execution, bilateral cooperation had been proceeding in a smooth and fruitful way, and reached the anticipated results.

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 China. 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. In contrast to wet 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 2010, the project, entitled "Cooperative Development of Dry FGD Byproduct Resource Comprehensive Utilization key Technology And Core Equipment", was initiated with the objectives to get a thorough understanding of byproduct characteristics and to advance dry FGD byproduct utilization. The three-year project was carried out by LETC with financial support of the Ministry of Science and Technology of the People's Republic of China, Other participants of the project include Green Byproduct Consulting Company LLC, OSUCOE and UK/CAER in the US .

Progress and achievements of the project is discussed below..

The Sino-American Flue Gas Cleaning Byproduct Resource Utilization Research Center

The research center was established by LETC in 2009. It has undertaken the above international and other projects and developed a variety of ways to utilize dry FGD byproducts, as shown in Figure 1.

A specialized laboratory was built for dry FGD byproduct characterization and utilization evaluation with focus on building materials applications. The laboratory possess state-of-the-art instruments for characterization and equipments for evaluation of utilization options of a specific dry FGD byproduct.

Figure 1 The Sino-American Flue Gas Cleaning Byproduct Resource Utilization Research Center

Achievements

Based on experience of project participants, it is to establish a platform specializing in dry FGD byproduct chemical and physical property characterization and a research center specializing in comprehensive utilization evaluation. Part of the core approach is to incorporate with the appropriate standards, technical specifications and guidelines, such as those in autoclaved brick, autoclaved aerated concrete, GGBS, mortars and cement etc., which has introduced in a previous paper[1]. A total of six national patents have been applied, five have been authorized.

Relying on enterprise cooperation for completion of two technical service contracts, we constructed an annual 120 million autoclaved brick production line with annual consumption of over hundred thousand tons of dry FGD byproduct demonstration line in Jilin Petrochemical in Jilin, China, and completed autoclaved aerated concrete block, mortar and GGBS production lines for dry FGD byproduct utilization demonstration and promotion with annual consumption of 80 thousand tons of dry FGD byproduct in r Meishan Steel in Nanjing, China.

Basic Properties of the Dry FGD Byproduct

Dry FGD byproduct is defined as the product that is produced from dry FGD systems, including CFB-FGD, SDA, NID etc., and consists primarily of calcium sulfite,, calcium sulfate, fly ash, portlandite and calcite.

Dry FGD byproducts can have different physical properties, elemental and mineralogical compositions depending on their source. It can be divided into three major categories: CFB Boilers, pulverized Coal-fired Boilers and iron and steel sintering plants.

More details about dry FGD byproduct compositions and properties was reported in a previous paper[2]. In summary, it is a solid byproduct with a low moisture content (<2%), fine particle size d50 between 15 and 30 microns depending on fly ash content), various ratio of calcium sulfite, calcium sulfate, fly ash, portlandite and calcite., depending on its source.

Application Cases

Petro China Jilin Petrochemical Company Second Power Plant

Petro China Jilin Petrochemical company has a fly ash autoclaved brick production line. Since 2012 LECT had been working with Jilin Petrochemical company to use dry FGD byproduct from its coal-fired power plant as raw material f to produce autoclaved brick. Because of the high content of fly ash in dry FGD byproduct as shown in Table 1, it has high potential for use in production of autoclaved brick . Although the elemental compositions are similar with fly ash, As shown in Figure 2, it was difficult to mold and serious cracks were appeared after autoclave using dry FGD byproduct directly. This could be caused by the relatively high sulfur content and fine particle size distribution (d50 about 30 microns).

After modifying e mix formulation and operating parameters of brick machine, autoclaved brick with 30% dry FGD byproduct addition was produced successfully in the second half of 2013 All the brick properties meet the National Standard. The mix formulation and operating parameters are shown in Table 2.

Table 1 Major elemental compositions of byproduct from Jilin petrochemical company

Sample	SiO_2	Al_2O_3	K_2O	MgO	CaO	Fe_2O_3	Na_2O	SO_3	LOI
1#	54.54	24.88	2.17	1.17	5.48	4.21	0.78	2.07	3.2
2#	57.91	24.29	2.40	1.17	4.56	4.28	1.08	1.79	1.23
3#	30.28	12.14	1.31	0.85	25.11	2.73	0.58	14.38	11.81

Figure 2 Mold difficulty and appearance ofserious cracks after autoclave when using dry FGD byproduct directly

Table 2 The formulation and the main parameters of brick machine

Formulation	Pound fly ash	Dry FGD byproduct	Quick lime	Gypsum	aggregate
Percentage	26.58%	27.03%	8.79%	1.57%	36.04%
Mixing time				3 min	
Depositing time				2.5 to 3.0 hrs	
Humidity before molding				10.5%	

Parameters of brick machine						
	air exhaust time/ s			Compress time / s		
Pressure	1st	2st	3st	1st	2st	2st
19 MPa	0.03	0.03	0.05	0.10	0.20	0.16

Meishan Iron & Steel Co., Ltd.

Meishan Iron & Steel Co., Ltd is a subsidiary of Baosteel Group Corporation (hereinafter referenced as Baosteel) which is the second largest iron and steel enterprise among the world. In 2008, LECT and Baosteel began to collaborate on flue gas desulfurization, the first project is Meishan Iron & Steel Co., Ltd which locates in Nanjing, Jiangsu, China. Along the Yangtze river, about 200 thousand tons of dry FGD byproduct produced from Baosteel. Under considerable pressure to go green, a technical service contact was signed between Baosteel and LECT with focus on dry FGD byproduct utilization in 2012. Considering about the short of construction materials in Yangtze river delta, autoclaved aerated concrete, GGBS and mortars are selected for utilization development.

As shown in Table 3, elemental compositions of dry FGD byproduct from Baosteel is different from that from Jilin chemical company. It has high calcium and sulfur and low fly ash contents. Taking consideration of the byproduct properties and marketing situation, the byproduct is used in autoclaved aerated concrete production replacing part of lime and gypsum, total addition ratio is about 5~10%. In addition, in order to improve the early strengths , about 5% of dry FGD byproduct was used in mix formulation for production of GGBS..

The final report was completed in 2013. As shown in Figure 3, a demonstration wall was constructed on--site by using autoclaved aerated concrete and mortar which contain dry FGD byproduct. With joint efforts of LETC and Baosteel, all byproduct had been utilized in 2014.

Table 3 Major elemental compositions of byproduct from Baosteel

Sample	SiO_2	Al_2O_3	K_2O	MgO	CaO	Fe_2O_3	Na_2O	SO_3	LOI
1#	0.67	0.34	0.39	1.70	48.06	0.34	0.11	32.86	/
2#	0.44	0.26	0.14	0.43	43.31	0.16	/	40.73	13.34

Figure 3 Construction of a demonstration wall onsite by using autoclaved aerated concrete and mortar which contain dry FGD byproduct

Summary and Conclusions

After completion of two technical service contacts, the project demontrated that it is feasible to utilize dry FGD byproduct commercially in china. In May 2014, the final technical report was finished, and approved by the Chinese Ministry of Science and Technology.

During t execution of the project, participants from China and the United States worked complementarily to make the project successful. The project has been progressed well during the implementation period. The planned goal of the project has been essentially accomplished. Dry FGD technologies have been emerging as technology-of-choice for multi-pollutants control of flue gas treatment. More new technologies for byproduct utilization should be developed to meet market demands and increasing dry FGD byproduct production in the future. International collaboration is beneficial for the future development.

Acknowledgements

The authors would like to acknowledge the Ministry of Science and Technology of the People's Republic of China for its financial support of the International Science & Technology Cooperation Program (Project No. 2010DFB93990), Jilin Chemical company and Baosteel group for its financial support for commercial development, UK/CAER and OSUCOE for their technical support.

References:

[1]. Su, Q., iang Y., Lu M., Chen Y,and Wu M. M., "Development of Dry FGD By-Product Utilization as Building Materials in China". World of Coal Ash (WOCA) Conference,May 22-25, 2013. Lexington, Kentucky, USA

[2]. Wu, M.M., Jiang Y.,Su Q.,Robl T.,Jewell R., Butalia T. S., Zhang Wand Wolfe W., "Dry FGD By-Product Characteristics and Utilization - International Perspective". , World of Coal Ash (WOCA) Conference2013, Lexington, Kentucky,USA