Development of Dry FGD By-Product Utilization as Building Materials in China

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ABSTRACT

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 and CFB boilers as polishing units in China. Major dry FGD technologies include circulating fluidized-bed gas desulfurization (CFB-FGD), spray dryer absorber (SDA), and NID processes. Compositions of by-products generated from these processes are similar except with different distribution of mineralogical components. The major sulfur-containing component in by-product is calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$).

In this paper, current status of development of dry FGD by-product utilization as building materials in China will be discussed. Building materials include autoclaved brick, autoclaved aerated concrete, mortar and others. Relationships of building material product quality with dry FGD by-product compositions, mix formulations, production procedures, operational conditions and others will also be discussed.

INTRODUCTION

As a new type by-product, the increasing volume of dry flue gas desulfurization by-product (DFGD) has presented disposal problems in China, due to potential groundwater contamination and landfill cost [1], [2]. About four million tons of DFGD was generated in 2012. The volume generated will increase substantially in the future. The utilization of DFGD is clearly a better alternative for disposal.

DFGD exhibits physical and chemical properties different from other coal combustion by-products (CCBs). It has high amounts of calcium- and sulfur-containing components. The major sulfur-containing component in DFGD is calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$). The utilization of DFGD is related to its physical and chemical properties, which are often site-specific and can be affected strongly by coal types, flue gas compositions, unit operations and other factors. As mentioned previously [3], there are published reports of DFGD applications in building materials, such as autoclaved brick [4], aerated autoclaved concrete[1], cement [5], [6] , ground granulated blast furnace slag

(GGBS)[7], mortar[8] and others in China. However, most of these applications are scattered, in small scales or lack of systematic evaluation.

Lonjing Environment Technology Co. Ltd (LETC) has established an Engineering and Technology Research Center to develop DFGD utilization, since 2011. A large number of DFGD generated from different sources have been collected, classified and characterized. DFGD include those generated from coal-fired power plants, iron and steel sintering plants, CFB boilers, and other industrial installation. For high volume and everlasting uses, the utilization is emphasized on production of building materials. The relationships of building material product qualities with DFGD compositions, mix formulations, production procedures, operational conditions and others are being evaluated systematically to combine research with utilization development. Results of some studies are discussed below.

RESULT AND DISCUSSION

Characterization of DFGD

Physical Properties

Comparing with SEM imagery of DFGD from coal-fired power plants and iron and steel sintering plants (Figure 1), the former generally contains spherical fly ash particles, while the latter is irregularly shaped and not spherical, there are more fly ash collected downstream into FGD system as part of DFGD in power plants than in sintering plants.

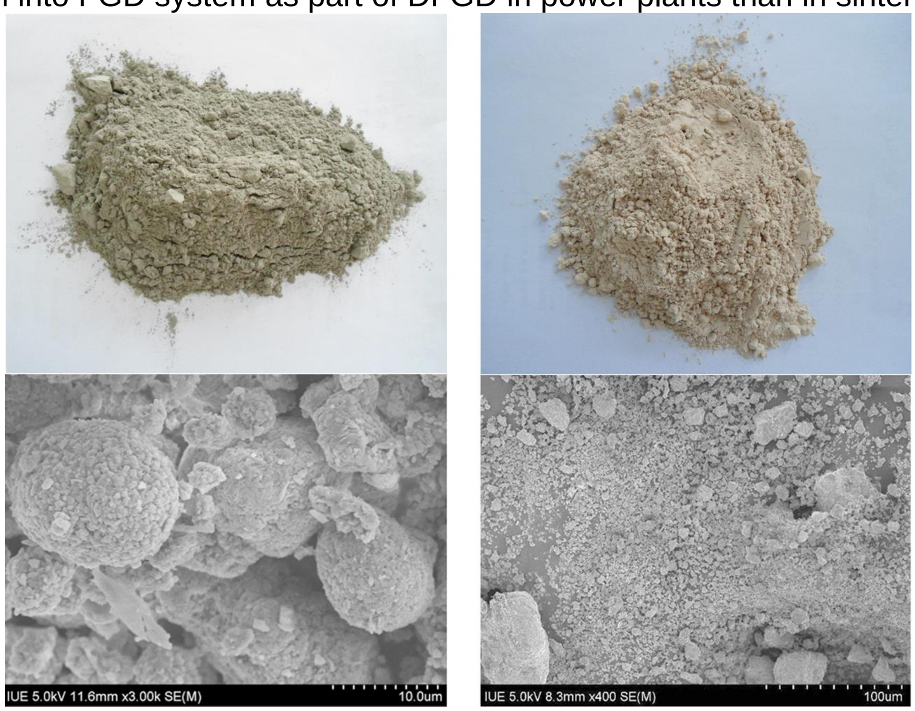

Figure 1 SEM Imagery of DFGD from Power Plants (left) and Sintering Plants (right)

Particle size distributions of DFGD were analyzed using a laser particle size analyzer for comparison (Figure 2). The results indicate that DFGD samples had a D_{10} particle size of less than or equal to 5.0 μm, a D_{50} particle size of 10 to 20 μm and a d_{90} of 50 to 120 μm. The more fly ash contains in the samples, the larger are mean D_{50} and D_{90} particle sizes.

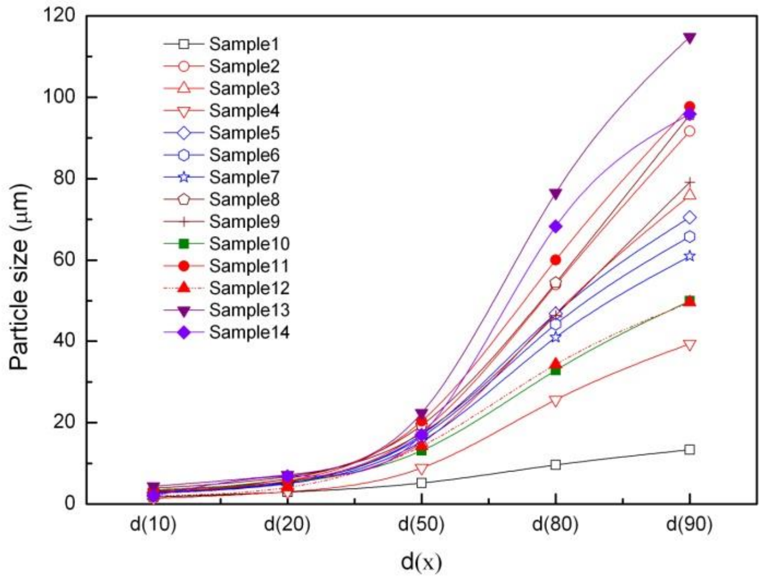

Figure 2 Particle Size Distribution of DFGDs

<u>Chemical Properties</u>

The major elemental composition of DFGD samples were characterized by X-ray Fluorescence (XRF) spectroscopy. The elemental composition (Si, Al, Fe, Ca, S) are reported in oxide form. As shown in Figure 3, the fly ash components, consisting mainly of SiO_2, Al_2O_3 and Fe_2O_3 in DFGD, are higher in power plants than those in sintering plants. This is related to collection efficiency of ash pre-collection equipments (baghouse or ESP) before desulfurization systems.

The major mineralogical compositions of DFGD were determined by X-ray diffraction (XRD) and thermogravimtric analysis (TGA), which indicate that the major sulfur-containing component is $CaSO_3 \cdot 1/2\ H_2O$. The amount of $CaSO_3 \cdot 1/2\ H_2O$ is higher in DFGD generated from sintering plants than from power plants.

All these physical and chemical properties can affect mix formulation, production procedures, operational condition and others for DFGD utilization.

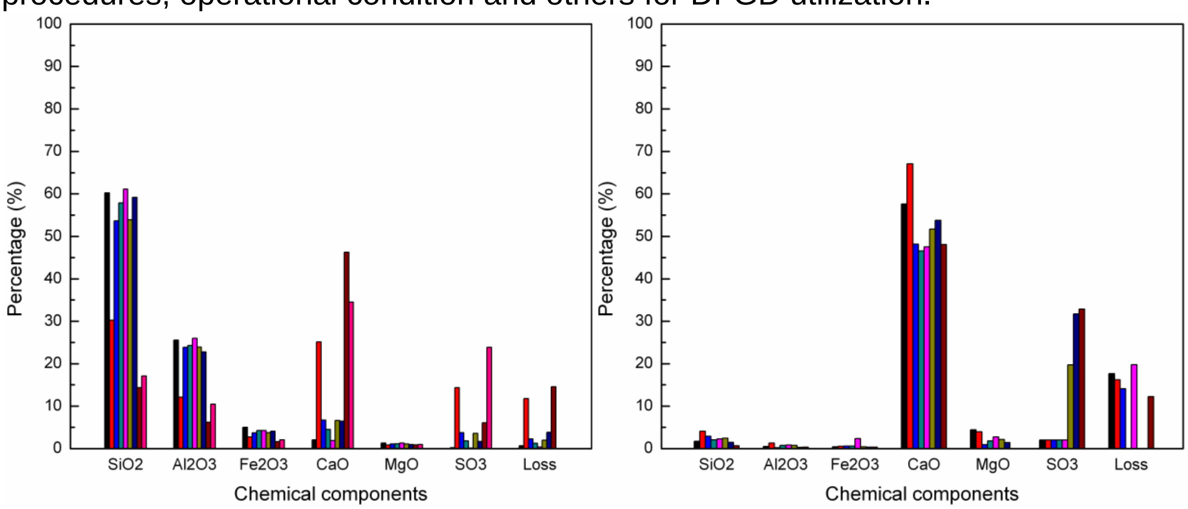

Figure 3 Elemental Compositions of DFGD from Power Plants (Left) and Sintering Plants (Right)

Autoclaved Brick

Bench Scale Production

Materials and formulation: the materials used include Mei-Steel sintering plant's DFGD (CaO 48.06%, SO_3 32.86%, SiO_2 and Al_2O_3 1.01%), fly ash (SiO_2 48.43%, Al_2O_3 21.58%, Fe_2O_3 4.58%), hydrated lime ($Ca(OH)_2$), and sand. A series of mix formulations with 40% DFGD addition were designed with different ratios of water and ash, mixing method, ratio of fly ash and hydrated lime.

Prepare methods: mix components were blended and dry mixed for 1min, and then wet mixed for 2min. the mixture was introduced into a brick mold (240mm*114mm), and then compressed by hydraulic press with pressure increase rate 4kN/s to produce shaped product for autoclave.

Discussion

According to the National Standard Requirements, the compressive strength should be greater than 15MPa, the freeze and thaw resistance test should be conducted more than 15 cycles; the requirement is more stringent in cold weather areas. The brick quality is related to grain composition, water addition, mix formulation, and engineering parameters. An optimum grain composition is beneficial for high strength and low shrinkage. Water addition is one of the crucial factors in mix formulation. A proper addition is important for optimum compaction, Figure 4 illustrates the influence of water addition on brick dry density and strength; there is a positive correlation of dry density and strength with increasing water addition within the adequate range. An optimum ratio of siliceous material (fly ash) and calcareous material is beneficial to maximize DFGD addition and brick quality due to formation of stable minerals, such as tobermorite, during autoclave. As shown in Figure 5, when added quantity of cementations material (cement or hydrated lime) is 10%, in order to meet the M20 standard and high freeze and thaw resistance requirements, the Si/Ca ratio should higher than 1 for cement and at least 2 for hydrated lime. In formulation with cement addition, strength development is mostly from cement hydration and partly from the reaction between cement hydrate product lime and silicon/alumina oxides. In formulation with lime addition, strength development is all from the reaction between lime and silicon/alumina oxides during the autoclaved phase.

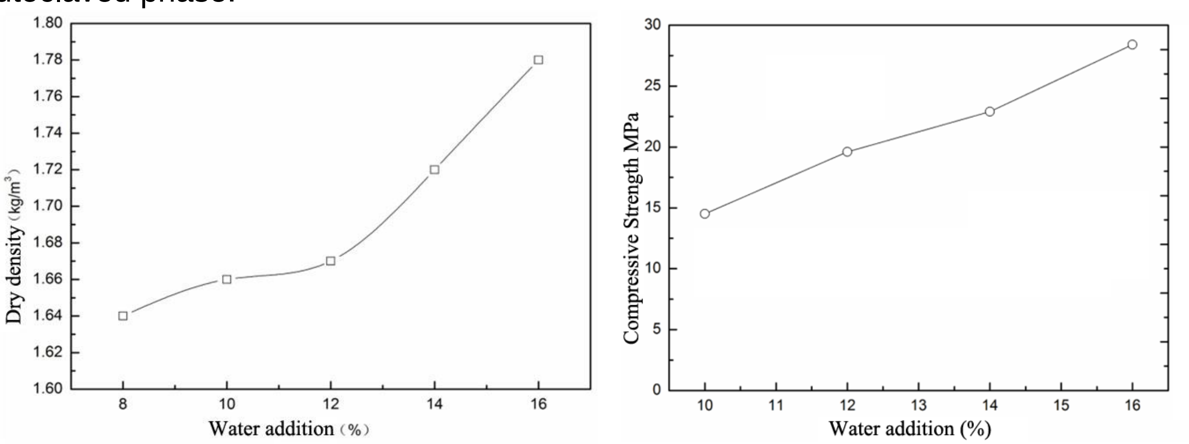

Figure 4 The Dry Density and Compressive Strength of Bricks with Various Water Addition

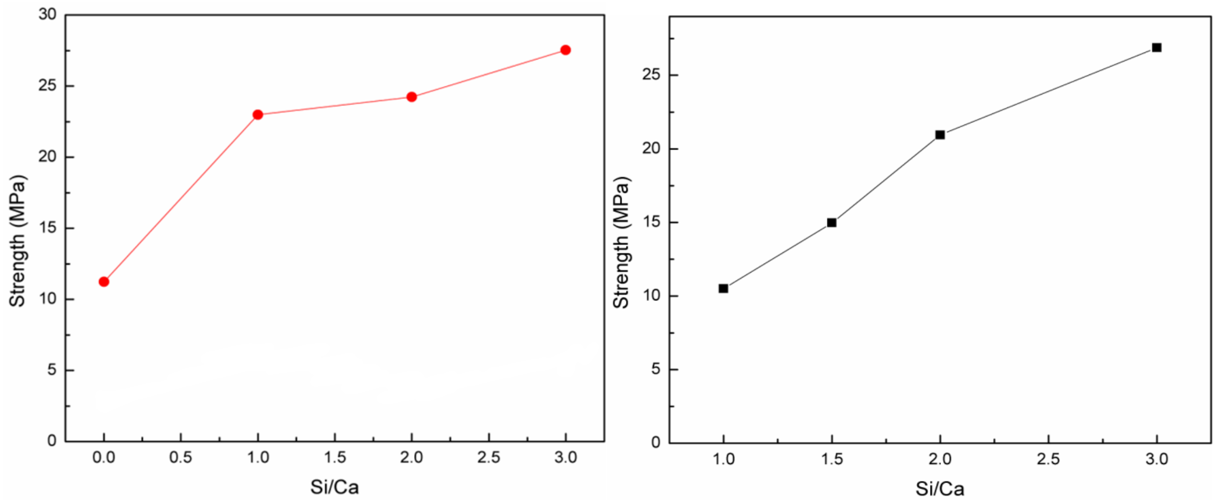

Figure 5 The Compressive Strength of Brick with Different Si/Ca (fly ash/cementitious material)

<u>Pilot Plant and Commercial Production</u>

Autoclaved brick with low DFGD addition (below 20% by weight) has been produced commercially in MINXIN and CHUANGZHAN brick production plants, in Fujian and Guangdong province, respectively. Pilot plant study of autoclaved brick production is currently being conducted with higher DFGD addition (higher than 30% by mass) by LETC in SHENGYUE brick production plant, Jilin province. Figure 6 shows autoclaved brick being produced in the production line with 30% DFGD addition. The pilot plant study is expected to be completed soon.


Figure 6 Brick Production in SHENGYUE Pilot Plant Study

Autoclaved Aerated Concrete

<u>Bench Scale Production</u>

Materials and formulation: the materials include Mei-Steel sintering plant's DFGD (CaO 48.06%, SO_3 32.86%, SiO_2 and Al_2O_3 1.01%), fly ash (SiO_2 48.43%, Al_2O_3 21.58%, Fe_2O_3 4.58%), lime, Portland cement and aluminum (Al) powder. A series of mix formulation with different amounts of DFGD addition were studied. The influence of gypsum was also examined.

Prepare methods: Mix components were blended for 1min except cement, lime and Al powder, and then cement/lime added and mixed for 2min. Al powder was added 30 seconds before finishing. The mixture was introduced into a mold, the knockout time is 5 hours, and then autoclaved for 6 hours at about 1.3MPa steam pressure.

Discussion

Quartz sand or fly ash, lime, cement, gypsum, and water are used traditionally for production of autoclaved aerated concrete. DFGD can be used as mix component due to its compositions (contain fly ash and hydrated lime) and can function as gypsum replacement.

DFGD from Mei-Steel was used as feed material of autoclaved aerated concrete. Figure 7 illustrates the influence of DFGD addition on product density and strength. The cementitious materials (cement and hydrated lime) used were reduced from 30% to 25% with increasing DFGD addition. As shown in the figure, when DFGD additions are lower than 20%, the dry density and strength can meet the standard B06 and A3.5 requirements. When the DFGD additions are higher than 30%, the dry density and strength cannot meet simultaneously. Mix formulation need to be readjusted for further development.

Gypsum is added in small quantities to optimize properties of autoclaved aerated concrete. With proper DFGD addition, gypsum addition is not required. As shown in Figure 8, gypsum can enhance the strength greatly without DFGD addition. However, both strength and dry bulk density are not affected, if 20% DFGD is added to replace gypsum and part of fly ash.

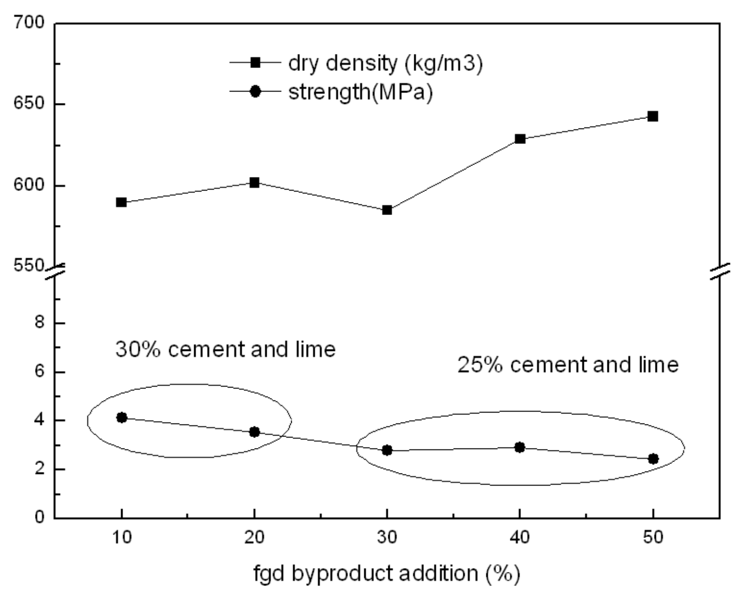

Figure 7 The Effect of DFGD Addition

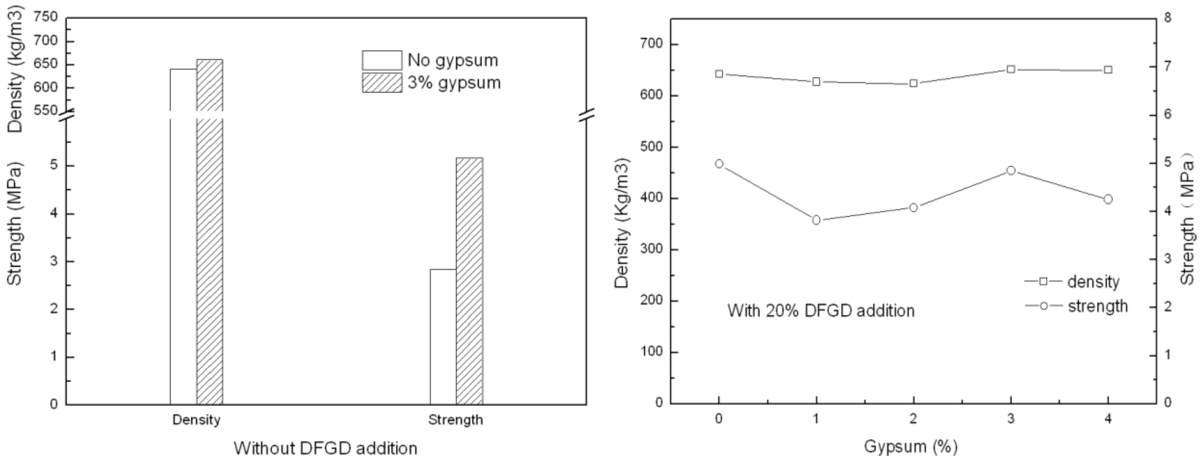

Figure 8 The Effect of Gypsum on product quality with or without DFGD Addition

<u>Pilot Plant and Commercial Production</u>

Pilot plant test was conducted in HONGTAIXIN, Fujian province. About 15% DFGD was added in mix formulation. Figure 9 shows production using DFGD as a feed material. As a substitute for gypsum, a lower DFGD addition (5~10% by weight) was used to produce autoclaved aerated concrete commercially in HENGDA and KUNLONG, Anhui province.


Figure 9 Autoclaved Aerated Concrete Production in HONGTAIXUN Pilot Plant

Ground Granulated Blast Furnace Slag (GGBS)

GGBS is made by quenching molten iron slag from a blast furnace in water or stream, to produce a glassy, granular product that is then dried and ground into a fine powder. GGBS is used to make quality-improved slag cement in combination with ordinary Portland cement, which has been widely used in Asia, particularly in Japan and China. DFGD can be use in GGBS as admixture, due to its fine particle sizes and cementitious properties.

Quality of GGBS with 2% to 10% DFGD addition was evaluated in bench scale testing. Test results are listed in Table 1. Comparing with commercial GGBS, addition of DFGD reduces the 28d strengths slightly and still can meet the standard requirements, when added dosage is lower than 10% with Power plant DFGD and 5% with sintering plant

DFGD. The 7d strengths are significantly increased which can benefit concrete early strength. However, it should be pointed out that GGBS with DFGD addition has longer setting time than that of commercial GGBS. Which need to be solved in the further study.

Table 1 Comparing of DFGD-GGBFS with Commercial GGBFS

Samples		**7d activity index* (%)**	**28d activity index* (%)**	**Ratio of fluidity (%)**	**setting time (min)**
Standard s95		75	95	95	600
Control		100	100	100	327
Commercial GGBS		71.76	108.98	105	396
Power plant	4%DFGD	94.95	106.33	103	670
	6%DFGD	100.63	104.27	101	696
	8%DFGD	98.70	104.61	101	626
	10%DFGD	98.72	102.03	97	608
Sintering plant	2%DFGD	89.70	107.35	103	588
	3%DFGD	91.66	102.79	101	595
	4%DFGD	97.64	105.74	101	588
	5%DFGD	102.39	101.25	97	606

Note: *means the compressive strength ratio of samples and control.

Commercial Production:

Addition of DFGD in GGBS as a mix component is commercially processed in JINSHICHUAN GGBS plant, Nanjing. Figure 10 shows the DFGD was transported by a tank car to JINSHICHUAN plant.

Figure 10 Use DFGD as Mixture in JINSHICHUAN GGBS Plant, Nanjing

Mortar

Mortar is a workable paste used to bind construction blocks together or plaster a wall. Mortars are typically made from a mixture of sand, a binder such as cement and lime, and water. According to the China regulations, on-spot mixing is forbidden, due to the environmental pollution. DFGD as a dry and fine material with proper compositions can be used as a mix component in mortar. DFGD addition can have positive effects on increasing mortar strength, and water retention, and on decreasing density, as shown in

Table 2. For instance, 10% DFGD addition in mortar improved the strength from 7.4 MPa (without DFGD) to 8.85 and 10.03MPa for Mei steel plant and Mei power plant DFGD, respectively. Water retention rate increases from 85.93% to 88.70% and 94.17%, respectively. However, the effect of prolong setting time should merit serious attention. It should make sure that the maximum setting time of mortar is less than 24 hours during application.

Table 2 Properties of Mortar with Different DFGD Additions

Samples	**DFGD addition**	**Setting time**	**Density kg/m^3**	**Strength Mpa**	**consistency mm**	**Water retention rate %**
Control	0	10h	2047.5	7.40	64	85.93
Mei steel plant	8.4%	12h6min	1895.5	/	100	88.69
	10%	12h	1890	8.85	100	88.70
	11.1%	12h7min	1865.5	6.51	98	88.10
	12.5%	12h40min	1866	5.90	106	89.27
Mei power plant	8.4%	17h36min	2023.0	9.89	74	90.70
	10%	18h50min	2016.5	10.03	75	94.19
	11.1%	18h37min	1999.5	5.98	86	89.68
	12.5%	17h40min	2018.0	6.32	95	92.05

Commercial Application:

DFGD generated from SAN Steel plant in San Ming, Fujian Province has been packaged and sold to customer as a mix component of plaster mortar. Figure 11 is one corner of DFGD packaged factory in SANMING, Fujian province.

Figure 11 One Corner of DFGD Packaged Factory

Cements

Literature reports indicate that results on evaluating effectiveness of DFGD as cement retarder are inclusive. For instance, Yang et al[9] reported that DFGD cannot be used as cement retarder alone, because calcium sulfite in DFGD is not effective on prolonging the cement setting time. In contrast, Su et al[10] reported that DFGD can prolong cement clinkers with high C_4AF contents due to the reaction between calcium sulfite and C_4AF, forming monosulphoaluminate (AFm). The effectiveness for retardation appears related to compositions of both cement clinker and DFGD.

In the study at LETC, we choose four clinker samples and five DFGD samples with different sulfur contents, range from 2.43% to 16.31, for comparison. The elemental compositions of clinkers are shown Table 3.

Table 3 The Elemental Compositions of four Clinkers

Samples	Compositions /%						parameters		
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	KH	n	P
Lantian	21.560	5.030	2.680	66.640	-	0.825	0.94	2.80	1.88
Tianyu	17.510	5.540	3.130	66.610	-	2.830	1.11	2.02	1.77
Huarun	21.100	4.690	3.430	65.320	-	1.450	0.94	2.60	1.37
Xinlong	20.910	4.190	3.110	67.580	-	0.989	1.01	2.86	1.35

The influence of added DFGD samples on clinker setting times are compared as shown in Figure 12, Although the mechanism has not yet been identified, results indicate that most of DFGD samples can prolong the cement setting times. All the final setting time can meet the standard (lower than 600min), mostly between 200 to 400 min, except TIANYU clinker which is between 80 to 160 min.

It is note worthy to mention that the setting times of Huarun or Xinlong clinkers with added Liaoyang DFGD are prolonged first and then shortened with increasing amounts of DFGD addition.

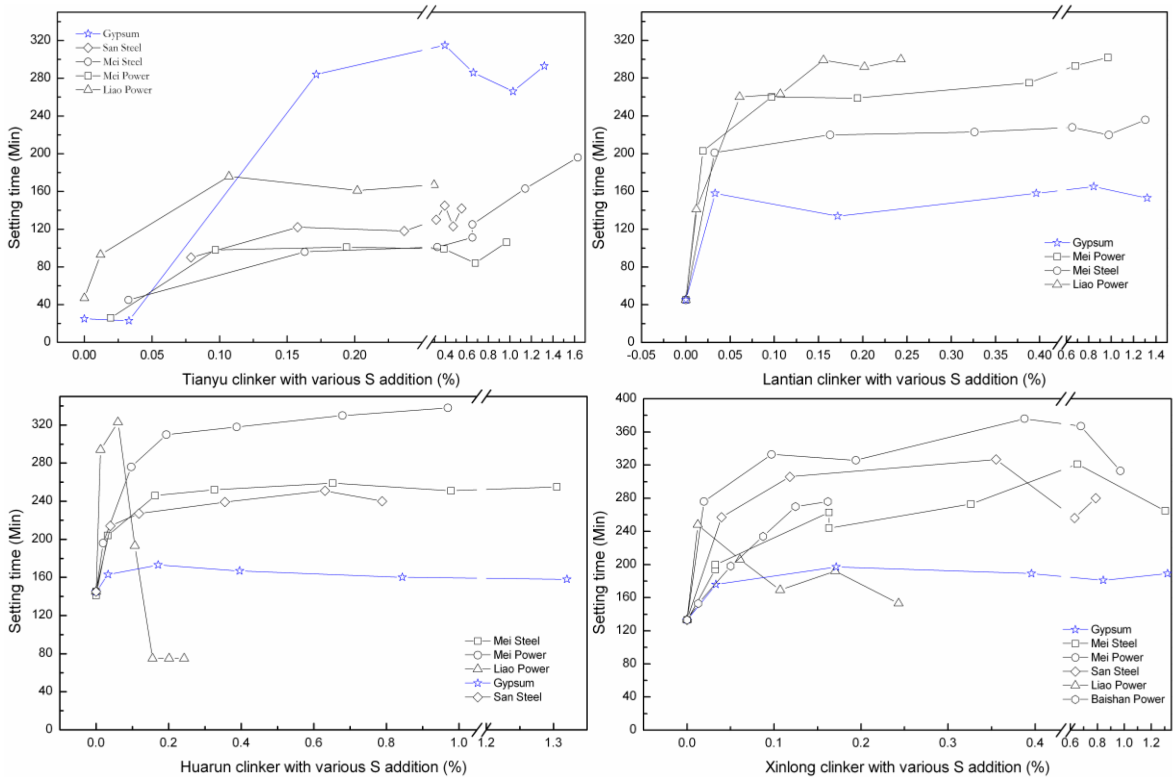

Figure 12 Comparison of Various DFGD and Gypsum Addition as Retarders on four Clinkers

The stability and strength are also evaluated on TIANYU clinker in comparison with those in gypsum, as shown in Figure 13, the use of DFGD as cement retarder does not affect the stability or strength development. The stability was examined by both Le chatelier and pat tests, a series of strength testing with different DFGD addition on four clinkers are being carrying out to compare with gypsum with clinkers. So far, all test results can meet the standard requirements.

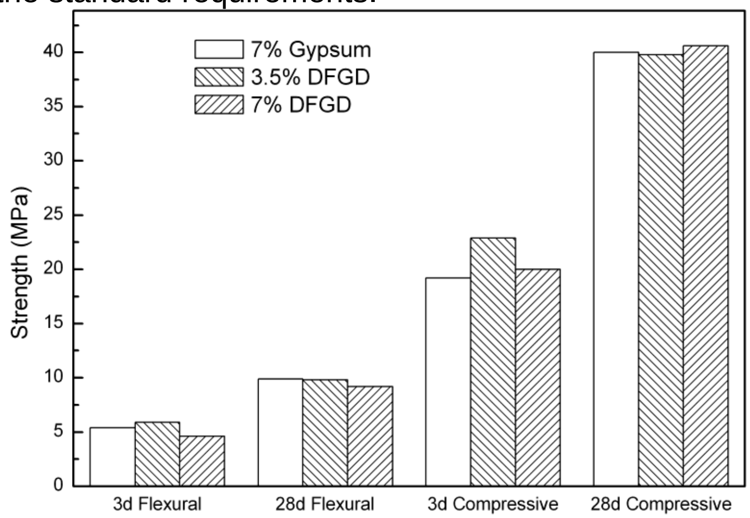

Figure 13 The Effect of Added DFGD on Cement Strength Development (TIANYU Clinker)

Conclusions

As discussed above, it is feasible to use DFGD as a mix component in building materials, such as autoclaved brick, aerated autoclaved concrete, cement, mortar, GGBS and others. Some of these have already commercialized in China. However, it is important to evaluate the effect of DFGD characteristics on production of building materials. More systematic studies are needed to combine DFGD characteristics with utilization to advance commercialization.

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