Advances in Utilization of Flue Gas Desulfurization Gypsum

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Abstract: A large number of coal-fired flue gas is the culprit that caused by air pollution and acid rain. Based on this reason, lime/limestone-gypsum wet flue gas desulfurization(FGD) process as the main desulfurization technology are used by most countries to control emissions of SO_2,at the same time generating a huge amount of flue gas desulfurization gypsum。This paper describes the physical and chemical properties of natural gypsum and FGD gypsum， reviews the utilization of experience and research status and progress of FGD gypsum. Our country FGD gypsum problems in the application process is also pointed out.

INTRODUCTION

China's energy structure shown in Table 1, coal as the first energy of China's economic development, accounts for the proportion of China's energy consumption about 70%, much higher than other countries. Coal-based resources also determined the energy production of coal in China's dominance status will be continue for a long period of time. According to the statistics that 80% of China's coal consumption is directly used for combustion, coal-fired power plants in which more than 50% of coal consumption accounts[1]. SO_2 gas as one of the major air pollutants facing mankind today, which is mainly caused by coal-fired flue gas massive emissions(sulfur in coal is the main cause of the presence of large amounts of SO_2 in the flue gas), SO_2 emissions 90% comes from coal-fired. Lots of SO_2 gas emissions in the air, it will enter the human respiratory system and cause great harm on human health , and reacts with O_2 and H_2O in the air forming acid rain, which have an impact on the human environment and socioeconomic and endanger human survival and development.

Table 1. China's energy structure

Year	Total energy consumption （10,000 tons of standard coal）	Coal/%	Oil/%	Natural gas/%	Others/%
2010	324939	68.0	19.0	4.4	8.6
2011	348002	68.4	18.6	5.0	8.0
2012	361732	66.6	18.8	5.2	9.4

Source: China National Statistics Yearbook

In order to solve the problem of pollution caused by SO_2 emissions and to control coal-fired flue gas emissions, countries have enacted policies requiring to the new power plants which must be matched desulfurization equipment, and in the production of generator sets retrofitted desulfurization unit. In the last 1970s, china began to study the thermal power plant flue gas desulphurization (FGD) technology, then began to large-scale application FGD equipment in coal-fired power plant to control SO_2 emissions. After nearly 30 years, China's FGD technologies, especially wet FGD technology made great progress, and began to use in the market widely.

However, due to a large quantity of FGD gypsum emissions (for example, in 2011, the total emissions of up to 67.7 million tons[2]), utilization levels for FGD gypsum is not high, coupled with abundant resources of natural gypsum, which lead to low utilization of FGD gypsum and resulting in a lot of stockpiled. If the large accumulation of solid waste disposed improperly, it can cause serious harm, such as the occupation of the land, soil pollution, water and air pollution, endanger human health and form secondary pollution[3]. As people gradually deepened understanding FGD gypsum, many scholars began carried out extensive research and application work for its utilization, a large number of experimental studies shown that FGD gypsum can be used instead of natural gypsum. From the perspective of protecting the environment from pollution and save the limited natural gypsum resources, FGD gypsum can produce good social and economic benefits.

GYPSUM AND NATURAL GYSPUM PERFORMANCE COMPARISON

FGD gypsum is also called chemical gypsum, the major component is calcium sulfate dihydrate ($CaSO_4.2H_2O$), which is a industrial by-product gypsum collected by the FGD apparatus, and its physical and chemical properties have a common law of natural gypsum, after conversion can also get five patterns and seven kinds of morphological variants.

As an industrial by-product gypsum, FGD gypsum also has some properties of chemical gypsum, usually contains about 8%~12% attached water, particle size distribution is relatively concentrated, with a diameter between 30~60 μm, the value of pH is generally around 5~9[2]. In addition, its physical properties and chemical composition (natural gypsum case in Shanxi Xishan mine) compared to natural gypsum is quite different, as shown in Table 2 and Table 3 below.

Table 2. Physical properties of natural gypsum and FGD gypsum contrast [2,4,5]

Materials	Color	Size	Polymorph	Impurities
Natural gypsum	White or colorless transparent	About 140 μm	Diamond thin plate-like, columnar or needle	Clay, sand, etc.
FGD Gypsum	Yellow, nearly white or grayish black	Less than 60 μm, generally between 30 ~ 60 μm	short column, the process is unstable spherical, flaky	ash, calcium carbonate, calcium sulfite and Mg, K, Na, Al, etc.

Table 3. compare the chemical composition of natural gypsum and FGD gypsum [2,4] /%

Materials	SO_3	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	H_2O	$CaSO_4.2H_2O$
Natural Gypsum	44.17	31.75	1.34	0.14	0.18	0.98	19.69	82.56

FGD Gypsum	40.0～46.0	31.0～45.0	1.5～6.0	0.1～2.2	0.1～1.2	0.2～0.7	15.0～21.0	≥90

As shown in Table 2 and Table 3, there are some differences in color, Polymorph, particle size and impurities with natural gypsum, but the chemical composition of both are very similar, and content of $CaSO_4.2H_2O$ overall higher than natural gypsum, its provide a theoretical possibility for large-scale substitute natural gypsum. In addition, the mechanical properties(in the low moisture), frost resistance, thermal properties,water and water vapor transport parameters are very good [5].

CURRENT RESEARCH STATUS OF FOREIGN STUDIES

German FGD Gypsum Research and Application Status

Germany is one of the earliest countries that development and application of FGD gypsum, from the late 1970s and early 1980s, Germany begun research and develop FGD gypsum utilization technology, formed a relatively complete research, development and applications system, which is one of the world's most developed countries that comprehensive utilization of FGD gypsum. July 1, 1983, "The Federal Pollution Prevention Act", paragraph 13 (large combustion plant regulation GFAVO) become effective execution, since 1st July 1988, the large combustion device that thermal power more than 300MW (120MW equivalent electric power plants) released flue gas SO_2 content shall not exceed 400mg/Nm3, sulfur content must be less than 15% of the sulfur content of the fuel[6-7]. After the entry into force of this Act, Germany began to invest a lot of money in a short time to install FGD equipment for its domestic thermal power plants and large coal-fired equipment, currently there are more than 90% of German coal-fired boiler with FGD equipment, 80% of FGD equipment generate gypsum.

German FGD technology is mainly divided into three kinds(additives, wet and dry), which in the power plant adoption rate up to 86%, only about 2% of the other, and there are about 90% of FGD installations use lime/limestone-gypsum FGD technology, 75% of industrial plaster from FGD gypsum[1]. Germany is a major producer of FGD gypsum in Europe, its production accounts for about 1/3 of the whole of Europe, 1993 FGD gypsum production in Germany was 3.2 million t, 1995 reached 5 million t, 1999 reached 5.7 million t, 2000 the annual output is 6 million t, the actual utilization of FGD gypsum reached 5 million t, 2004 actual utilization reached 6.2 million t. FGD gypsum is a major gypsum resources in Germany, accounting for over 75% of the total production of gypsum[6-7].

Japan FGD Gypsum Research and Application Status

Japan is the world's first large-scale application of FGD equipment countries, which uses wet limestone-gypsum desulfurization unit more than 75% of total installed capacity. Because of Japan's domestic natural gypsum resources are very scarce and the great demand for gypsum, so Japan attaches particular importance to the comprehensive utilization of industrial by-product gypsum. Early in 1955, has been successfully achieved commercial scale use of industrial by-product gypsum. Before 1988, domestic gypsum raw materials is the main source of phosphogypsum, the production declined since 1989, FGD gypsum replace phosphogypsum became a major source of gypsum in Japan.

According to statistics, from 1987 to 1999, Japan's annual FGD gypsum production remained at around 2 million t, 2001 Japan FGD gypsum production was 1.7 million t, the actual use of 1.5 million t, utilization is 88.24%. FGD gypsum utilization rate over 90% in Japan, the main application areas are gypsum board and cement retarder, where gypsum used in cement industry the FGD gypsum accounted for 30% to 40%[8].

Table 4. FGD gypsum production in Japan (1987-1999)

Year	1987	1991	1995	1996	1997	1998	1999
Yield（10,000 tons）	172.7	201.6	213.6	212.1	216.1	224.3	231.6

United States FGD gypsum Research and Application Status

The United States is the world's second-largest FGD gypsum producing countries, the early 1990s, the United States FGD gypsum production is about 2 million t, only to replace natural gypsum below 5%. In the 1990s, FGD gypsum began to be widely used throughout the gypsum manufacturing, and large quantities of replacing natural gypsum. FGD gypsum production in the United States in 2000 was 9 million t, increased to 12 million t in 2006, of which about 9.05 million t get used, utilization rate up to 75.4%. In 2009, the United States FGD gypsum production has reached 13.5 million t, the yield of FGD gypsum is sustained growth, according to the experts predict that the United States FGD gypsum production will reach more than 20 million t by 2015. The main application of United States FGD gypsum is mixed with natural gypsum to produce gypsum board, cement retarder and building plaster, accounting for about 90% of the total utilization of FGD gypsum, in which the amount of FGD gypsum plaster board production consumes up to 70% and only 5% for the cement industry. In recent years the development of low-cost production of α-plaster and other new technologies, it will be extended to the use of self-leveling FGD gypsum plaster, gypsum mine, fillers, protective coatings, etc.[9].

DOMESTIC RESEARCH STATUS

China power plant FGD equipment adopted only a short period of time, the use of advanced technology, costly lime/limestone-gypsum wet FGD technology is began to the 1990s. Due to the lime/limestone-gypsum wet FGD technology application in china comparative success, resulting in production of FGD gypsum rapid growth in China. The Table 5 and Figure 1 shows china's SO_2 emissions, FGD gypsum output and variation trend in recent years.

Table 5. SO_2 emissions and FGD gypsum output

Product / Year	Sulfur dioxide (10,000 tons)	FGD gypsum (10,000 tons)	Utilization /%
2007	2468.1	1700	-
2008	2321.2	3500	-
2009	2214.4	4300	56
2010	2185.1	5230	69
2011	2217.91	6770	71

Source: China National Statistics Yearbook

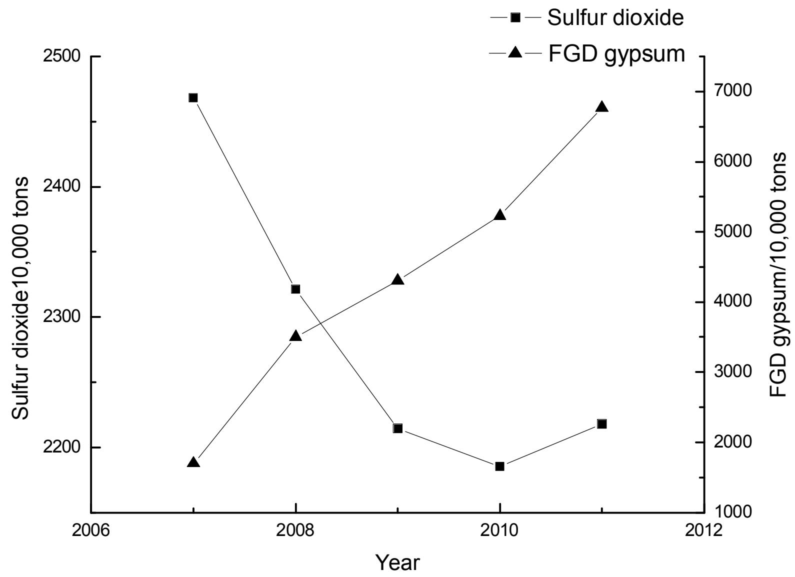

Fig. 1. SO_2 emissions and FGD gypsum yield variation trend

Domestic FGD gypsum comprehensive study on the application of technology from the 90s of last century, after 20 years of effort, has made a considerable part of the research results.Domestic utilization of FGD gypsum mainly in the following aspects.

(1) cement industry: In the cement, usually need to adding a certain amount of gypsum to adjust the setting time of cement, therefore, FGD gypsum can be used instead of natural plaster as cement retarder. Guo Dajiang[10], SHI Huisheng[11] studied the possibility of using FGD gypsum instead of natural gypsum as cement retarder, analyzed FGD gypsum and natural gypsum chemical composition, thermal properties, mineral composition, micro-structure and other properties, preparation of FGD gypsum as cement retarder, study the effects of different FGD gypsum content on the performance of cement and concrete. Experimental studies shown that using FGD gypsum for the production of cement retarder, the experimental data are in line with national standards, can effectively adjust the cement setting time and workability of concrete is good, compared with natural gypsum as cement retarder, the cement performance is consistent and replacing natural gypsum as cement retarder is feasible.

But as the use of cement retarder, gypsum dosage is generally about 3%~5%, relatively low dosage. Combined with FGD gypsum instead natural gypsum, the need for the existing cement production equipment for system transformation, the use of FGD gypsum in cement is not very optimistic.

(2) Preparation of gypsum board: FGD gypsum another important way is to be used to produce various kinds of gypsum plasterboard. Many scholars use FGD gypsum mixed with fly ash, slag, reinforcing fiber and other admixtures prepared of various types of gypsum board, the indicators in line with national standards. Xue Lili[12] and others use non-calcined gypsum, fly ash and slag as a cementitious material, incorporation of lime, alkali-activated materials and early strength agent, stir and then add the waste glass foam particles by mixing molding, preparation of gypsum-based insulation board have good performance. Thermal conductivity is 0.08~0.15W / (mK), compressive strength can reach more than 0.5MPa, dry apparent density is a minimum of 611kg / m^3.

Preparation of gypsum plaster board is widely used, the technology is relatively mature, but china is rich in natural gypsum resources and mining large, coupled with the FGD gypsum performance is unstable, resulting in China's current gypsum board production enterprises use of FGD gypsum is not very common.

(3) Preparation of composite binder: The use of FGD gypsum, fly ash, slag, cement and other cementitious materials preparation of composite cementitious materials is a major way to achieve substantial use of FGD gypsum. Peng Jiahui, Lin Fanghui[13] calcined FGD gypsum to anhydrite at 600℃~ 900℃electric furnace, they use anhydrous FGD gypsum and fly ash as the main raw material, composite alkaline activator and small quantities of accelerators early strength agent formulated a good performance, excellent strength and water resistance of the new plaster fly binder can be used for the production of light wall materials. Lei DongYi[14]and others prepared gypsum-based high-strength cementitious using undisturbed gypsum as raw material, slag and cement as active admixtures, lime and water glass as alkaline activatorhave, the cementitious good mechanical properties, 28 d compressive strength over 42MPa.

Preparation of composite cementitious materials, gypsum dosage is generally more than 40%, can solve problems of stockpiling. However, due to the application of technology is not mature enough, domestic gypsum based composite cementitious materials on application examples in the actual project is not common.

(4) others: In addition to more than a few ways can also be used to produce a variety of gypsum products, such as gypsum block, mortar, wall insulation materials, building plaster, wall plaster, etc. Apart from this, can used to prepare self-leveling material, used as a soil conditioner and mine filling materials. Although the range of applications is wide, utilization comparison is still very low.

PROBLEMS OF FGD GYSPUM USE IN CHINA

China comprehensive utilization of industrial solid waste, especially the level of utilization of FGD gypsum with a big gap compared with developed countries in the world. There is a whole, China's comprehensive utilization of gypsum is not very high and there are still some problems in the process of comprehensive utilization solved urgently.

(1) Comprehensive utilization rate is low. According to statistics, China's comprehensive utilization of FGD gypsum in 2010 was 69%, in 2011 reached about 71%, utilization of other industrial by-product gypsum is lower. Maximum utilization of FGD gypsum is used as cement retarder, some of the high added value products, such as gypsum board, gypsum powder, self-leveling plaster and other products are still gaps[4].

(2) Utilization technology for FGD gypsum needs to be improved. There are more types of products, but the technical content and application level is not high, the lack of independent intellectual property rights, high value-added utilization of technology and equipment, some utilization of advanced and applicable technology promotion is not enough, lagging industrial applications.

(3) Quality and stability of the FGD gypsum needs to be improved. Quality and performance of the power plant gypsum produced larger changes, it is mainly for the high moisture content, excessive harmful ingredients, which seriously affected the enthusiasm of enterprises to use FGD gypsum[1].

(4) Unbalanced regional development, policy support is insufficient[2-3]. There is considerable geographical factors which influence the level of use of FGD gypsum, Beijing, Shanghai and some other economically developed areas and urban centers close to 100% utilization, and some economically underdeveloped areas and natural resource-rich province of gypsum restricted price, market and other factors, the comprehensive utilization rate is very low. Government should take

measures from the policy and economic perspective to increase the utilization of industrial by-product gypsum support and accelerate the promotion of advanced and applicable technologies, and draw attention to the market for gypsum utilization, and to improve the comprehensive utilization of FGD gypsum.

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