# Analysis on Chimney Inner Wall Anti-corrosion in GGH Eliminated Wet Desulfurization System

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Abstract: This paper discusses on the physicochemical mechanism of chimney corrosion in wet desulfurization. Gas temperature, internal pressure and structure defects of chimney are pointed out to be the main factors. According to these factors, various methods about treating chimney anti-corrosion at home and abroad are also indicated. Moreover, we propose an anti-corrosion plan which based on comparing anti-corrosion mechanism, construction methods and construction periods of anti-corrosion methods.

Keywords: Wet Desulfurization, GGH, Chimney inner Wall Anti-corrosion, physicochemical mechanism

### **1 INTRODUCTION**

Along with development of electricity industry in china, the environmental pollution becomes more and more severe, thus the environmental protection standard is upgraded in recent years, for example, power plant SO<sub>2</sub> emission must below 400 mg/m<sup>3</sup> constructed in third period<sup>[1]</sup> and flue gas must be desulfuried either from new or old boiler. Nowadays, the sulfur removal is mainly classified into wet desulfurization and dry Desulfurization, wet Desulfurization systems are typically installed in units larger than 200 MW. Chimney corrosions which seldom studied and do not have any specific anti-corrosion stipulation in design standards in our country are usually concerned in Wet Limestone/ Lime-Gypsum Desulphuration, a mature technology <sup>[2,3]</sup>. Therefore, the study of anti-corrosion should according to the national conditions and advanced experiences of other countries.

### 2 INFLUENCE OF DESULFURIZATION TECHNICS ON CHIMNEY CORROSION

Typically the temperature of flue gas emitted from air pre-heater is 120 -140 which higher than acid dew point and will not condensation in tail duct and Chimney inner Wall. Otherwise, If the temperature of flue gas is lower than acid dew point, especially emitted from GGH eliminated system (only about 45 ), the condensation will occur, which is the main reason for chimney corrosion. Moreover, internal pressure and structure defects are also responsible for chimney corrosion.

## **3 MAIN FACTOR FOR CHIMNY CORRSION**

### 3.1 Production of Corrosive Medium

After wet desulfurization,  $SO_2$  and  $SO_3$  conversion in flue gas are 95 % and 20 % respectively. Moreover, there are other acid material, such as HF and HCl, when the temperature is below acid dew point, the flue gas will condensation and produced acid liquid will in turn attach on chimney wall. The temperature of wet Limestone/LimeGypsum Desulphuration absorber is calculated as:

$$P_{w} = P_{2} - P_{1}(1 - Y_{H_{2}O}) \left(\frac{273 + T_{w}}{273 + T_{i}}\right)^{\frac{k-1}{k}}$$
(1)

where  $P_w$  is partial pressure of water vapor contained in flue gas(mba),  $P_1$  and  $P_2$  are outlet and inlet pressure of absorber(mba),  $Y_{\rm H_2O}$  is the water content in initial flue gas (%),  $T_i$  is inlet temperature of absorber ( ),  $T_w$  is the saturated temperature of flue gas, k is the adiabatic exponent of flue gas, k=1.14 in generally.

Typically, the saturated temperature of outlet absorber is 40 -50, which is lower than dew point, 40 -60, thus the flue gas will condensation when flowing through chimney. Due to the existence of SO<sub>3</sub>, the acid dew point temperature of chimney can be calculated as <sup>[4]</sup>:

$$t_{\rm ld} = 186 + 20 \log[{\rm H_2O}] + 26 \log[{\rm SO_3}] \tag{2}$$

where  $t_{ld}$  is the acid dew point temperature, H<sub>2</sub>O is the water vapor concentration by volume, SO<sub>3</sub> is the SO<sub>3</sub> concentration by volume.

Acid dew point temperature is often 100 -150 from equation (2), whereas the outlet temperature of Wet Limestone/Lime-Gypsum desulphuration are typically 80 and 40 -50 with and without GGH. It can be conceived that the corrosive medium will effuse whether the GGH is installed, and the condition is worse when the GGH is eliminated.

#### 3.2 Chimney Internal Pressure

In addition to gas temperature, another important factor is chimney internal pressure. When the chimney is operated on a positive pressure, the corrosive medium will effuse to surface of reinforced concrete cylinder through cracks in the Inner Walls, the same phenomena will not occur in negative pressure operation. For GGH eliminated wet desulfurization system, the flue gas temperature is relatively low, thus the gas density and positive pressure zone will expands. Figs.1 and 2 demonstrate the distribution of static pressure before and after desulfurization system equipped. [5]



#### 3.3 Structure defects of chimney

If there are cracks or defects exist in the inner Walls of chimney, the corrosive medium will effuse to lining materials through these defects under a positive pressure. This condition will more serious in penetrated crack which may destroy the chimney.

#### **4 CHIMNEY ANTI-CORROSION**

The chimney anti-corrosion measurements are different from each other and it mainly depends on wet desulfurization system with or without GGH.

GGH is a heat exchanger which lower the temperature of initial flue gas and higher the temperature of purified flue gas. For GGH equipped wet desulfurization system, the outlet temperature is higher than 80 which lower than acid dew point and higher than dew point, thus the high concentration  $H_2SO_4$  will be produced and not seriously erodes chimney. In addition, the higher temperature will reduce the zone of internal positive pressure, hence the produced  $H_2SO_4$  will not effuse to lining material of chimney. Therefore, the chimney of newly power plant only needs take commonly anticorrosion measurements, for example, use acid-proof bricks. For GGH eliminated wet desulfurization system, the outlet temperature is only about 45 which lower than both acid

dew point and dew point, thus the low concentration  $H_2SO_4$ will be produced and seriously erodes chimney. Moreover, the lower temperature will expand the zone of internal positive pressure, hence the produced  $H_2SO_4$  will effuse to lining material of chimney. Therefore, both new and old builds must take anti-corrosion measurements.

### 4.1 Anti-Corrosion in Foreign Country

Chimney design mainly divided into two categories for GGH eliminated wet desulfurization system. The first one is equipping wet stack onto absorber or emitting the purified flue gas through cooling tower, these measurements are commonly adopted in foreign country (typically for newly constructed power plant), for example, most GGH eliminated wet desulfurization system in German are using this plan. The second one is taking anti-corrosion treatments such as acid-resistant glass brick technologies, anti corrosion of alloy materials, anti corrosion of glass flake, anti corrosion of VP and anti corrosion of polyurea. These measurements are successfully applied in foreign country, especially for nickel-based alloy which have great technical advantages but relative high expenses.

#### 4.2 Anti-Corrosion in China

Due to the technical constrict of our country, there is seldom application of equipping wet stack onto stack or emitting the purified flue gas through cooling tower. The main measurements adopted in our country are anti-corrosion treatment on chimney. According to the 10.2.2 clause of chimney design code (GB50051-2002) and 7.4.4 clause of power plant civil engineering structure design code (DL5022-93), multi-cylinder or bushing type (outer cylinder and inner cylinder are separated) chimney should be adopted when the outlet flue gases are Strong Corrosive. Meanwhile, chimney is required by power industrial standard when the boiler of power units is larger than 600 MW. Hence, multi-tube or bushing type chimney is mostly adopted in the newly developed power plant larger than 600 MW units. Old plant innovation and small or middle power plant construction projects are still single-cylinder concrete structure type. These two types (single-cylinder and multi-cylinder) will be introduced as following.

## 4.2.1 Multi-cylinder or Bushing Type Chimney

According to previous reference, multi-cylinder or bushing type chimney has following advantages:

(1) Exhaust pipe and bearing pipe are separated with each other, thus bearing pipe will not be eroded.

(2) Every boiler has exhaust pipe, hence single exhaust pipe fault will not influent other boiler.

(3) Flue gases will exert less influence on environment, because total number of chimney is reduced

(4) Have good running and management conditions. The chimney is maintained by elevator, thus other cylinders will not be disrupted.

Due to these obvious advantages, the multi-cylinder or

bushing type chimney becomes more popular in recent years. There are three primary anti-corrosive measurements for this kind of chimney: (1) inner cylinder is formed by anticorrosive materials, for example, foaming acid resistant brick (developed by Henkel), which have high acid resistance, high temperature tolerance, low thermal conductivity and low thermal expansion coefficient characteristics. Acid resistant brick is very commonly used in overseas (8 in Asia pacific, 45 in north America, 21 in Europe), but seldom applied in china.(2) Spraying flake resin and rubber lining on chimney inner wall. This technics are usually applied in absorber, but seldom used in chimney. (3) Line titanium plate on chimney inner wall. This technics has applied in Hou shi power plant (6×600 MW power units), Zhang zhou city, and Chang shu power plant (2×600 MW power units), Jiang Su province. The application of titanium plate is limited by its high expenses.

#### 4.2.2 Anti-corrosion of Single Cylinder Chimney

Nonmetal materials are usually adopted in anti-corrosive of single cylinder chimney. Due to the continual high temperature of rubber and glass flake lining, ageing and carbonization of organic materials and adhesive force of anti-corrosive materials and concrete, the service life of desulfurization island is typically about 5-15 years which shorter than its expected life, 25 years. Hence, the lining material must be frequently replaced and the investment will be expanded to about 2-3 times. Anti-corrosion is a bottleneck for developing GGH eliminated wet desulfurization in china. In the following paragraph, the novel anti-corrosive technics will be introduced. VP lining material application is realized by cooperation of Chongqing Dazhong company and Blome company. VP is a novel polymer which synthesized with a creative method (fill the inorganic particles into polymer base, then various super high molecular weight and high ordered polymers are composed), thus it has many advantages, such as acid and temperature resistance, thermal insulation and long service life. A special technics (GLT) should be adopted for VP lining material. This technology is different from traditional lining technics and realized by spraying the VP on surface of concrete or stainless with special device, hence it provide a effective anti-corrosive lining material to horizontal flue gas duct.

Various constructed materials, such as carbon steel, brick-plate or concrete can be sealed or repaired by VP lining material, the disadvantages of reduction of chimney inner diameter can be conquered by reasonable construction.

VP liner is constructed with 2–3 layers in chimney. The inner layer is a temperature and acid resistant film which have a great ability for resistant various inorganic acids, such as HCL, dilute  $H_2SO_4$  and  $H_3PO_4$  and excellent bond strength with concrete and stainless steel. The film is flexible in -51 –165.6 and performed excellent in practical application, due to its thermal insulation ,acid resistance, temperature resistance and eliminating stress between upper rigid cement and basic layer in high temperature. The outer layer (including surface and midst layer) is a modified polymer

powder and is constructed by means of GLT. The polymer can be used as acid-resistant lining materials for chimney and container et al. and especially adapts for the high temperature resistance, anti acid and anti water vapor. Moreover, the polymer has characteristics of heat insulation, thus it will guarantee the security of inner film under high temperature, for example, 1.5 inch polymer can guarantee 250 discrepancy between working face and its back. Up to now, although VP is a high performance material for chimney anti-erosion, there is no industry application in china. Its economical and technical feasibility need further verifying. According to reference, by adopting VP technics, a project of 210 meters chimney anti-erosion need about 45 days which is a relative long period. In addition, due to the technics and materials import, the expense is relative high, 1800 yuan/m<sup>2</sup>.

Recently, another anti-erosion technics (modified bi-component polyurea coat) is introduced by CALINDA company. The coat possesses high performance of chemical and abrasive resistance. Its working temperature is up to 180 (in some case 260). The specific parameters of polyurea coat are listed in the following table.

Table 1 Typical parameters for construction			
Parameters	units	Datum	
coating temperature of material B		60-71	
coating temperature of material A		60-71	
viscosity of material A	cps	500	
viscosity of material B	cps	500	
mixing ratio(A:B)		1:1	
gel time	seconds	6-10	
	seconds	<25	
spray pressure	psi	>1500	

Table 1 Typical parameters for construction

 Table 2
 Physical properties of coat

Parameters	Datum	Testing standards
shore hardness	65D	ASTM D2240
tensile strength (psi)	2750	ASTMD412
Elongation (%)	250	ASTMD412
tear strength	475	ASTMD624
Modulus(psi), 100 %	1610	ASTMD412
Modulus(psi), 200 %	2010	ASTMD412
humidity(per value)	<0.1	ASTME9680
adhesive force between steel and coat (psi)	>1500	ASTMD4541
adhesive force between concrete and coat (psi)	900	ASTMD4541

Notes: above datum are obtained from laboratory, testing results in practical application may be varied with varing construction technics and condition

medium	rate	medium	rate	
20% agetic agid	P	MgCl solution	Δ	
	D C	Mg(OH)	A	
AICL solution	т		A	
AICI3 Solution	I V	ng Mathanal	A	
liquid ammonia	Λ		C	
NH <sub>4</sub> OH solution	Х	tone	С	
5% NaCl	Α	mineral oil	Α	
10% NaCl	А	benzene	С	
borax solution	А	Naphtha	В	
boric acid solution	А	Naphthalene	В	
butane	А	10% Nitric acid	С	
CaSO <sub>3</sub> solution	Α	oleic oil	В	
CaCl solution	Т	palmitic acid	Α	
CaOH solution	Α	perchlorethylene	С	
5 % Ca(ClO) <sub>2</sub> slolution	Х	Phenol	С	
<u> </u>	•	20 %phosphoric	Т	
$CO_2$	A	acid		
СО	Α	KOH solution	Α	
CCl <sub>4</sub>	С	Hydraulic Oil 500	С	
castor oil	А	sugar solution	Α	
1	v	20 % NaOH		
ary chlorine gas	А	solution	A	
	Х	46 % NaOH	А	
wet chlorine gas		solution		
100/150 abromio acid	Х	5% NaClO	C	
		solution	C	
CuCl solution	А	20% NaClO	Х	
CuCl <sub>2</sub> solution		solution		
Cyclohexylamine	А	liquid SO <sub>2</sub>	Т	
Ethyl Acetate	С	50% H <sub>2</sub> SO <sub>4</sub>	Т	
industrial alcohol	С	50%-80% H <sub>2</sub> SO <sub>4</sub>	С	
10% tannic acid solution	Α	H <sub>2</sub> SO <sub>3</sub>	Т	
Chlorofluorocarbons-11	В	tartaric acid	Α	
Chlorofluorocarbons-12	Α	Toluene	С	
Chlorofluorocarbons-22	С	trichloroethylene	С	
Chlorofluorocerhons 112	٨	sodium phosphate		
Chiorofiuorocarbons-115	A	tribasic	A	
Chlorofluorocarbons-114	Т	tung oil	В	
fuel oil	В	Turpentine	С	
gasoline	В	50 H2O	Α	
glue	А	hydrogen	Α	
Glycerol	А	JP-4	С	
20 % HCl solution	В	JP-5	С	
30 % HCl solution	Т	JP-6	Х	
A: no influence, B: may use, C: cant' use, T: must do some				
tests before use, X: no available date, cant' use.				

Table 3	Chemical	l resistance	of po	lyurea	for

Characteristics of CLINDA polyurea:

• No catalyst, fast curing, prompt spray molding on arbitrary surface without flow, only 5mins gel time.

· insensitive to humidity.

• 100% solid content, only one spray is enough to attain desired thickness.

• excellent chemical and physical properties: high

performance of anti erode, anti aging, abrasive resistance, flexibility, good thermal stability, capable of long-term use in 100 condition, 200 thermal shock tolerance.

• Excellent low temperature tolerance, below to -45 .

Spray and cast with complete set, easy construction, high efficiency, multi- switch pattern (spray and cast) equipped on set.

Various color products can be made by adding different pigments and fillers, also, the polyuea can be strengthened by short glass fiber.

The most significant advantage of polyurea is short period construction, for example, a project of 210 meters chimney anti-erosion need only 12 days which is suitable for old plant innovation (short time shutdown results in low loss). Moreover, the cost for construction is relative low, about 750 yuan/m<sup>2</sup>–800 yuan/m<sup>2</sup>. According to a 210 meters chimney anti-erosion project performed by CALINDA company in Tai yuan,Shan Xi province, the chimney has operated 3 months without any problem. This is the first time polyurea technic applied in china, the technical feasibility need further verification.

Table 4 lists technical comparison of various anti-erode technics.

 
 Table 4
 Technical comparison of various chimney anti-erode technics

Technics	difficulty	Construction	Shutdown	Cost	
		period (date)	(date)	Yuan/m <sup>2</sup>	
polyurea	Easy	About 12	14	750-800	
VP	Hard	About 45	47	1800	
glass	Variable	About 40	42	200	
flake	Vallaute	A0001 40	42	200	
Alloy	Special				
plate	tool is	20-30	22-32	12000	
liner	needed				
foaming					
acid	A061/	40.60	12 62	2000	
resistant	easy	40-00	42-02	2000	
brick					

### 5 CONCLUSIONS

Chimney anti erode is a novel technology which needs many engineering verifying in china. The material property, construction period and cost et al. should be considered in technic tests. Polyurea is thought to be a promising material, its technical and economical feasibility need further tests.

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