CEMENT PLANT ENVIRONMENTAL TECHNOLOGY FOR ACHIEVING HIGH SO_2 REMOVAL

Sara Safariyeganeh
sara.safariyeganeh@mecsglobal.com

Cary Joe Lovett, PE
joe.lovett@holcim.com

***Abstract* - The EPA has adopted revised emission limits to the National Emission Standards for Hazardous Air Pollutants (NESHAP) for the Portland Cement Manufacturing Industry and also revised emission limits to the New Source Performance Standards (NSPS) for Portland Cement Plants. These changes revise the emission limits for specified air pollutants for new and existing cement plants.**

The NESHAP regulations address the emission limits for materials such as mercury, total hydrocarbons (THC), hydrochloric acid (HCl), and particulate matter.

The New Source Performance Standards (NSPS) address particulate matter, opacity, nitrogen oxides (NOx), and sulfur dioxide (SO_2).

Herein, a case study is presented in which a novel environmental technology was utilized to help achieve greater than 90% SO_2 removal efficiency in a cement plant located in the United States. A slurry scrubber was specified for this application due to its unique ability to achieve high removal efficiencies for SO_2-rich waste gases, using a low cost reagent. Additional capabilities of this system specific to the cement industry are also discussed. These capabilities include: (1)hot gas quenching particulate removal; and (3) resistance to the corrosive, abrasive, and thermally intense environments often found in cement plants.

Keywords: cement, slurry scrubber, flue gas, reverse jet wet scrubber, SO_2 removal, scrubber, flue gas scrubbing, flue gas desulphurization, fgd.

I. INTRODUCTION

High levels of SO_x in the atmosphere have caused degradation of agricultural productivity and also health issues. In asthmatic people, high levels of SO_2 may cause breathing problems. Similarly, long term exposure to sulfur dioxide can cause respiratory illness, alterations in the lungs defenses and aggravation of existing cardiovascular disease[1]. Sulfur dioxide is also one of the causes of acid rain, which forms when SO_2 and NOx react with water, oxygen and other compounds in the atmosphere to create mild solutions of sulfuric acid and nitric acid. Acid rain acidifies soil, lakes, and streams and also harms plants and animals that live in these ecosystems.

[1] www.epa.gov

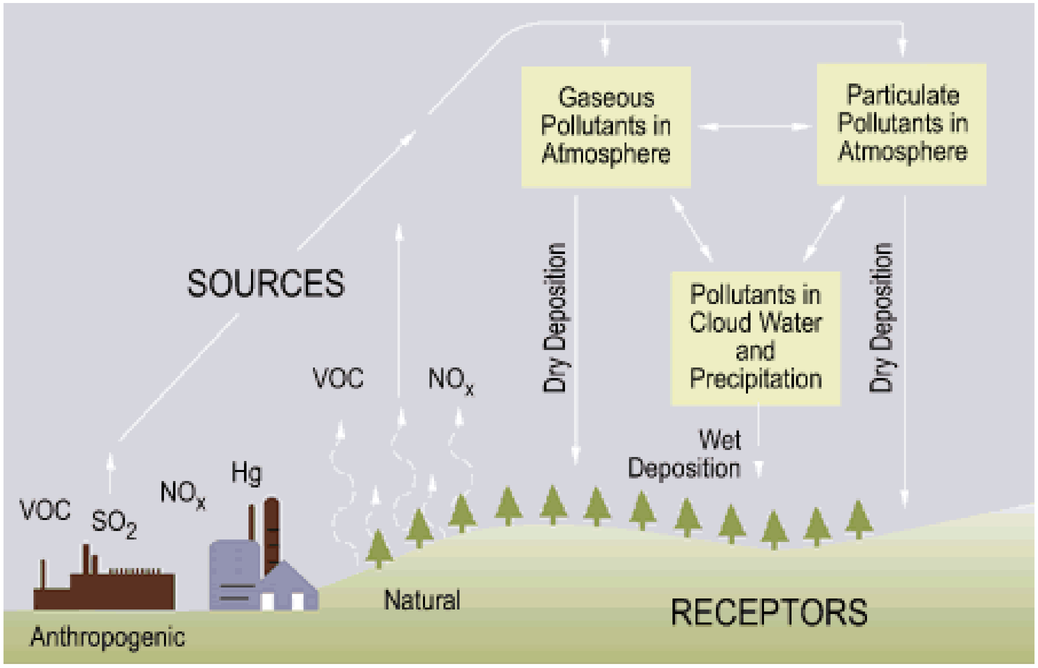

Fig. 1. Acid Rain (image from www.epa.gov)

II. BACKGROUND

During the production of cement, emissions of SO_2 are generated from the combustion and volatilization of sulfur compounds in the raw material and fuel. The SO_2 in the preheater reacts with $CaCO_3$ and returns to the kiln as $CaSO_4$. In the burning zone, some of the $CaSO_4$ is decomposed and will increase the SO_2 circulation in the kiln gas. The high sulfur content causes SO_2 emissions in the exit gas, choking of the preheater, and also formation of kiln coating rings. Even if a low sulfur content fuel such as natural gas is used, there are still SO_2 emissions from the preheater due to sulfides, such as pyrite and marcasite, in the raw material.

This paper discusses the operation and benefits of a wet slurry scrubber installed in a cement plant in the US to reduce the plant's SO_2 emissions. The scrubber treats gasses leaving the Preheater and Alkali ByPass systems. This specific cement plant uses coal, petcoke and tire derived fuel (TDF) as fuel, however the raw material (limestone) used by this specific plant has very high sulfur content.

The scrubber was built and has been in operation since 2001.

III. CASE STUDY

In order for a cement plant in the US to achieve the new SO_2 emissions standards, a wet scrubber was constructed.

Fig. 2. Slurry Scrubber

Two separate cases were evaluated: one with 15% Alkali By-Pass and the second case with 40% Alkali By-Pass. Additionally, the plant needed the capability to treat two separate gas streams. One gas stream was from the Preheater Outlet and the other is the Alkali By-Pass Exhaust. One gas stream contained HCl and the other contained NH3. These two streams could not be combined together since HCl and NH3 would react and produce submicron ammonium chloride which would cause opacity at the stack. Therefore, the scrubber was designed with two inlet barrels. Tables 1 and 2 below show the theoretical properties of the inlet gas to the scrubber:

Inlet Conditions	COMPOUND OPERATION				DIRECT OPERATION			
	Preheater			Bypass	Preheater			Bypass
	Minimum	Normal	Maximum		Minimum	Normal	Maximum	
Gas flow, Nm3/s wet	80	96.9	111.9	54.8	55.8	92.5	114	54.8
Gas flow, Nm3/h wet	288,000	348,840	402,840	197,280	272,880	333,000	410,400	197,280
Gas flow, m3/h wet**			647,219	370,207			822,888	370,207
Gas temperature, C	82	92	102	165	190	193	195	165
Composition, vol%								
N2		58.2	57.1	76.0		60.4	60.2	76.0
CO2		22.5	23.2	2.1		22.4	22.7	2.1
O2		7	6.4	18.9		7.6	7.4	18.9
H2O		12.3	13.3	3		9.6	9.7	3
SO2+HCl+NH3		<0.1	<0.1	<0.1		<0.1	<0.1	<0.1
Total		100	100	100		100	100	100

Gas flow, Nm3/h wet	COMPOUND OPERATION			DIRECT OPERATION			BYPASS		
	Preheater			Preheater					
	402,840			410,400			197,280		
	SO2	HCl	NH3	SO2	HCl	NH3	SO2	HCl	NH3
g/kg clinker	1.25	0.04	0.083	2.5	0.14	0.187	1.25	0.35	0
kg/h at 225,000 kg clinker	281	9	19	563	32	42	281	79	0
mg/Nm3 wet	698	22	46	1371	77	103	1426	399	0
ppmv wet	244	14	61	479	47	135	499	245	0

	TOTAL COMPOUND OPERATION			TOTAL DIRECT OPERATION		
	Minimum	Normal	Maximum	Minimum	Normal	Maximum
Gas flow, Nm3/s wet	134.8	151.7	166.7	110.6	147.3	168.8
Gas flow Nm3/h wet	511,200	546,120	612,000	467,280	530,280	607,680
Gas temperature, C	112	117	122	178	183	186
Composition, vol%						
N2		64.6	63.3		66.2	65.3
CO2		15.1	16.3		14.8	16
O2		11.3	10.5		11.8	11.1
H2O		8.9	9.9		7.1	7.5
SO2+HCl+NH3		<0.1	<0.1		<0.1	<0.1
Total		100	100		100	100

Gas flow, Nm3/h wet	TOTAL COMPOUND OPERATION			TOTAL DIRECT OPERATION			WEIGHTED AVERAGE 90:10		
	600,120			607,680			600,876		
	SO2	HCl	NH3	SO2	HCl	NH3	SO2	HCl	NH3
g/kg clinker	2.5	0.39	0.083	3.75	0.49	0.187	2.625	0.4	0.093
kg/h at 225,000 kg clinker	563	88	19	844	110	42	591	90	21
mg/Nm3 wet	937	146	31	1389	181	69	-	-	-
ppmv wet	328	90	41	486	112	91	-	-	-

Table 1. Kiln Operation with 15% Alkali By-Pass

**Actual gas volume corrected for elevation of 1536 m asl, operating temperature and assumed inlet pressure of 250mm

Without by-pass: molar ratio of NH_3 to Cl = 4.0 With by-pass: molar ratio of NH_3 to Cl = 0.8

Inlet Conditions	COMPOUND OPERATION				DIRECT OPERATION			
	Preheater			Bypass	Preheater			Bypass
	Minimum	Normal	Maximum		Minimum	Normal	Maximum	
Gas flow, Nm3/s wet	79.9	88.8	96.0	74.0	55.8	87.0	94.2	74.0
Gas flow, Nm3/h wet	287,640	319,680	345,600	266,400	200,844	313,200	339,120	266,400
Gas flow, m3/h wet**			555,255	530,731			679,965	530,731
Gas temperature, C	82	92	102	192	190	193	195	192
Composition, vol%								
N2		58.5	57.4	66.0		60.5	60.2	66.0
CO2		22.9	23.5	5.5		22.8	23.2	5.5
O2		7.4	6.8	14.6		7.9	7.7	14.6
H2O		11.2	12.3	13.9		8.8	8.9	13.9
SO2+HCl+NH3		<0.1	<0.1	<0.1		<0.1	<0.1	<0.1
Total		100	100	100		100	100	100

Gas flow, Nm3/h wet	COMPOUND OPERATION			DIRECT OPERATION			BYPASS		
	Preheater			Preheater					
	345,600			339,120			266,400		
	SO2	HCl	NH3	SO2	HCl	NH3	SO2	HCl	NH3
g/kg clinker	1.25	0.04	0.083	2.5	0.14	0.187	1.5	0.46	0
kg/h at 225,000 kg clinker	281	9	19	563	32	42	338	104	0
mg/Nm3 wet	813	26	54	1659	93	124	1267	389	0
ppmv wet	285	16	71	580	57	163	443	239	0

	TOTAL COMPOUND OPERATION			TOTAL DIRECT OPERATION		
	Minimum	Normal	Maximum	Minimum	Normal	Maximum
Gas flow, Nm3/s wet	153.9	162.8	170	129.8	161	168.2
Gas flow Nm3/h wet		586,080	612,000	467,280	579,600	605,520
Gas temperature, C	134	137	140	191	193	194
Composition, vol%						
N2		61.9	61.1		63	62.8
CO2		15	15.7		14.8	15.4
O2		10.7	10.2		11	10.7
H2O		12.4	13		11.1	11.1
SO2+HCl+NH3		<0.1	<0.1		<0.1	<0.1
Total		100	100		100	100

Gas flow, Nm3/h wet	TOTAL COMPOUND OPERATION			TOTAL DIRECT OPERATION			WEIGHTED AVERAGE 90:10		
	612,000			605,520			611,352		
	SO2	HCl	NH3	SO2	HCl	NH3	SO2	HCl	NH3
g/kg clinker	2.75	0.5	0.083	4	0.6	0.187	2.875	0.51	0.093
kg/h at 225,000 kg clinker	619	113	19	900	135	42	647	115	21
mg/Nm3 wet	1011	184	31	1486	223	69	-	-	-
ppmv wet	354	113	40	520	137	91	-	-	-

Table 2. Kiln Operation with 40% Alkali By-Pass

**Actual gas volume corrected for elevation of 1536 m asl, operating temperature and assumed inlet pressure of 250mm

Without by-pass: molar ratio of NH_3 to Cl = 4.0 With by-pass: molar ratio of NH_3 to Cl = 0.7

The Preheater and Alkali By-Pass Exhaust streams were treated in two separate inlet barrels, which share a common disengagement/oxidation vessel. Each barrel had a stage of acid gas removal using reverse jets that injects the reagent inside of the inlet barrel.

The slurry scrubber utilizes a series of non-restricting14 inch diameter Reverse Jet Nozzles, allowing routine operation without pluggage or downtime. The primary functions of the Reverse Jet are gas quenching and acid gas absorption. This design is very difficult to plug, even with slurry concentrations of 20wt% solids in the liquid.

Fig. 3. View through Reverse Jet Nozzle

This particular cement plant utilizes dust collected from the kiln system bag filter as a reagent to remove the SO_2 from both gas streams. Calcium carbonate in the dust must first be dissolved into the liquid before the acid-base reaction can take place. The dissolution of the calcium carbonate is often the limiting step in the overall conversion of SO_2 to calcium sulfite. After combining many of the intermediate steps, the overall net reaction is:

$$SO_2 + CaCO_3 \rightarrow CaSO_3 + CO_2$$

With the oxygen present in the gas, some of these sulfites will be oxidized into sulfates; forming a mixture of sulfates and sulfites in the liquid. This mixture is undesirable, as it causes scaling in the scrubber and it is very difficult to filter. To facilitate the disposal and handling of the by-products, the calcium sulfite must be further oxidized to calcium sulfate Therefore a blower injects approximately 2150 Nm3/hr of air into the sump of the vessel to complete the oxidation of the sulfites to sulfate.

$$CaSO_3 + \frac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4.2H_2O\ (gypsum)$$

After the sulfite oxidation, the synthetic gypsum that is formed can be reclaimed by de-watering and using it as a substitute for natural gypsum in the cement finish mill systems.

IV. GENERAL OPERATION

In this wet scrubber system (refer to Figure 4 below), contaminated gas enters the top of the Reverse Jet, located in an acid resistant alloy duct, and collides with the scrubbing slurry which is injected upward through the abrasion-resistant large bore injectors. A standing wave of highly turbulent flow, called the Froth Zone, is created at the point where the liquid is reversed by the gas. In the Froth Zone, a very high rate of liquid surface renewal efficiently cools the gas to its adiabatic saturation temperature and accomplishes SO_2, HCl, and particulate removal. The reagent slurry is pumped from the reagent storage vessel to the scrubber vessel sump under pH control to maintain optimum operating conditions for acid gas removal. A recycle line from the reagent feed line returns a large portion of the slurry to the storage vessel. The recycle method is used as an effective method of reducing the slurry from settling in the feed lines.

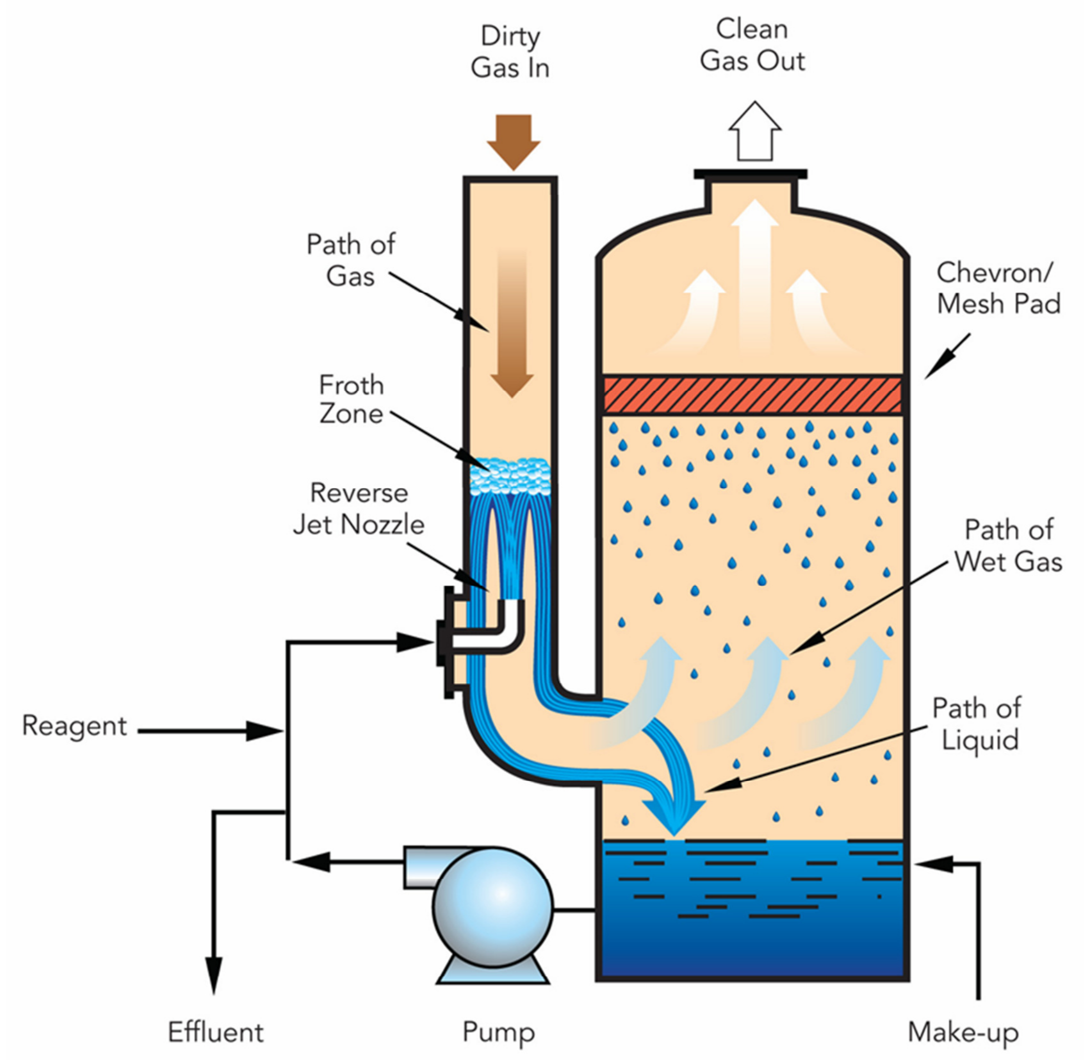

Fig. 4. Froth Zone in the Reverse Jet Scrubber

After passing through the Reverse Jets, the scrubbed gas exits the inlet barrel into the disengagement vessel, where significant levels of entrained liquids will be separated from the gas stream by impingement on the liquid surface. Finally, the cleaned gas will pass through a two-stage chevron entrainment separator with an intermittent water spraying system located near the top of the vessel for final separation of the gas and liquid. The cleaned gas exiting the scrubber will be mixed with hot exhaust from the clinker cooler in order to increase the stack temperature before being discharged to the atmosphere.

The hot gas entering the Reverse Jet will evaporate some liquid and the remaining liquid will flow into the disengagement vessel. This slurry then flows to the circulation pumps and is returned to the Reverse Jets. The liquid in the scrubber will run with a solids loading of approximately 20%. To avoid settling of solids, the liquid is recycled to the bottom of the sump to keep it agitated. The cement plant scrubber agitation system was constructed using a pump-around design which pumps slurry from the bottom of the vessel and discharges it through several nozzles located around the circumference of the tank. This keeps the slurry from settling in the bottom of the scrubber vessel. This pump-around design, however, requires maintenance on the piping due to abrasion. More-recently-designed slurry scrubbers use agitators instead of a pump-around. Agitators seem to be a much better option for keeping the slurry from settling in the sump, and eliminate the recirculation pipe abrasion problem. In addition, makeup water is automatically added to the system by level control to replace evaporation and effluent losses.

The cement plant has achieved greater than 90% removal efficiency of SO_2 in the scrubber, and an overall SO_2 removal efficiency through the entire process of over 98% in some instances. Sulfur enters the system as part of the raw materials and fuels, and is removed from the system through entrainment in the alkali bypass dust, being captured by the clinker, and through removal by scrubbing the flue gas stream in the scrubber.

The plant's overall efficiency in removing sulfur from the process is as follows;

	Sulfur Content (%)				Total Sulfur Input	SO2 Stack Emissions	Total Plant
	Raw Meal	Coal	Petcoke	TDF	short tons	short tons	Control Efficiency
2009	0.88%	0.46%		1.50%	13545	287.3	97.88%
2010	0.95%	0.46%	2.58%	1.50%	13903	277.3	98.01%
2011	1.00%	0.45%	2.58%	1.50%	12693	246.4	98.06%
2012	0.86%	0.46%	2.58%	1.50%	12129	297.7	97.55%

Table 3. Sulfur Removal Efficiency

V. CONCLUSION

Wet gas scrubbers can be designed to increase the removal of SO_2, HCl and particulate from gases leaving the cement plant. These scrubbers can also be designed so that the plant can use reagents readily available to them at the plant like CKD and limestone. The slurry scrubber operated at the referenced plant has proven to have a very simplified operation and has eliminated air pollution problems the plant was facing previously. Installing a slurry scrubber at a cement plant could also allow the plant to use fuels with higher sulfur content such as petcoke.