HCI Centrel for MACT Compleance

William Ciro, PhD, Cemex, and Melissa R. Sewell, Lhoist North America, discuss HCI control for NESHAP compliance at main and alkali bypass stacks using dry sorbent injection technology.

Introduction

Increasing regulation of the cement industry within the US is forcing many facilities to install emission control systems to reduce acid gases, including hydrogen chloride (HCl) and sulfur dioxide (SO_2) . One such regulation, issued by the Environmental Protection Agency (EPA) in December 2012, was the National Emission Standards for Hazardous Air Pollutants for Portland cement manufacturers (PC NESHAP). Beginning 9 September 2015, this regulation will require that Portland cement manufacturers reduce

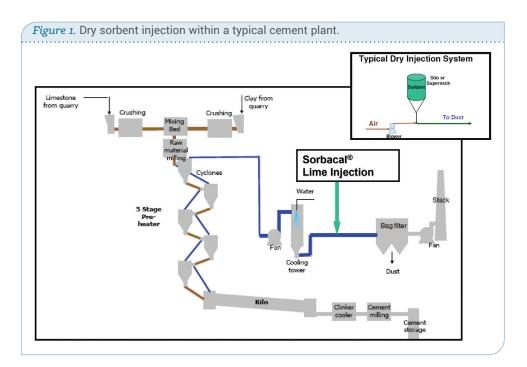
HCl emissions to 3 parts per million corrected to 7% oxygen. Lhoist North America and Cemex collectively worked on a trial programme to demonstrate HCl compliance at the main and alkali bypass stacks using dry sorbent injection (DSI) technology with hydrated lime (a calcium-based reagent). This article will discuss the trial programme, the technology selection and the results achieved at this facility and other Cemex plants where similar trial work has taken place.

The participants

Lhoist North America, part of the Lhoist Group, is a leader in calcium-based technology used in various flue gas treatment technologies. Lhoist's reagents are supplied in a number of wet limestone scrubbers, semi-dry absorbers (SDA) and most recently dry sorbent injection (DSI) systems within the coal-fired power sector, as well as in a number of manufacturing sectors; these include cement, chemical, paper and glass. This knowledge and experience was used in collaboration with Cemex, a worldwide leader in cement production and construction materials, in order to develop a successful compliance strategy for the upcoming PC NESHAP regulation.

The technology

The basic principle of flue gas treatment for acid gas is the neutralisation of acidic components such as SO_2 , SO_3 , HCl and/or HF, using alkaline reagents to form corresponding solid salts (such as $CaSO_4$, $CaCl_2$, Na_2SO_4 , NaCl, etc). These reactions can be accomplished by a number of technologies, including wet scrubbers, semi-dry adsorbers and dry sorbent injection (DSI) systems. Each technology has potential advantages and disadvantages but in many industries a low capital cost and low water-consuming technology is of utmost importance. Another key consideration in technology selection revolves around residue generation and reuse; within the cement industry, the compatibility of these reagents in the finished product



is of specific concern. Based on these factors and the successful experience in acid gas mitigation using this technology, it was determined that DSI with hydrated lime would be the optimal solution if PC NESHAP compliance for HCl could be demonstrated for various plant fuels, raw materials and process conditions.

Removal of acidic gas components takes place within DSI systems through the injection of a reagent as a dry powder into the flue gas, allowing chemical reactions between the gas and the reagent's surface.

Table 1. Summary of HCI demonstration tests using standard hydrate and Sorbacal® SP Demonstrated compliance with PC NESHAP 3 ppm limit for HCI						
	%		°F	tph	tph	%
Cemex Plant A main (raw mill down)	86	Baghouse	500	0.5	0.3	40
Cemex Plant A bypass	95	Baghouse	800	0.6	0.5	17
Cemex Plant B	84	Baghouse	540	0.5	0.3	40
Cemex Plant C	88	Baghouse	627	1	0.5	50
Cemex Plant D	63	Baghouse	535	1	0.4	60
Cemex Plant E	90	Baghouse	720	2	1	50

Reprinted from April 2014 World Cement HCl or SO_2 in the flue gas that comes into contact with the hydrated lime, either in-flight or in the particulate control devices, will follow these common reactions:

- Ca(OH)_{2(S)} + 2HCl_(g) ==> CaCl_{2(S)} + 2H₂O_(g)
- Ca(OH)_{2(S)} + SO_{2(g)} ==> CaSO_{3(S)} + H₂O_(g)

The reaction products, dust and excess additive require downstream filtration. Either sodium-based or calciumbased reagents can be used in DSI technology, but there are important considerations that must be kept in mind during the selection process; these include negative effects on residue generation and compatibility within the finished products, a main reason that this work's focus was only on calcium based reagents.

DSI systems using optimised hydrated lime offer the potential for a low capital cost solution while allowing for high removal performance of acid gases, including HCI. DSI is relatively easy to install and operate and is a completely dry process, resulting in dry residues and no water requirements. In addition, DSI systems require a much smaller footprint than many other types of technologies and typically require less lead-time due to the simplified equipment requirements.

Over the past few years there have been significant improvements in the performance of DSI systems, such that their overall reliability and availability have greatly increased. Concurrently, there have also been developments to improve the performance of some DSI reagents so that a given removal level can be achieved at lower dosage rates, or alternatively an improved performance can be achieved at a given dosage rate.

Factors that impact DSI effectiveness

The three major design and operating areas that impact the performance of a DSI system are summarised below.

Flue gas properties

The key flue gas properties of importance are the concentrations of acid gas species and moisture. The flue gas temperature at the point of injection is also a critical parameter in determining the effectiveness of DSI technology.

Understanding all of the acid gas species present in the flue gas is important in that the reagents react preferentially with the varying acid gas pollutants. Generally, calcium hydroxide (hydrated lime) will first capture SO_3 , then HCl, followed lastly by SO_2 . This means that when evaluating the amount of reagent required to achieve a given acid gas control level, the reagent utilised to capture the other pollutants must be considered. The temperature at the injection point is also important as, to a certain extent, specific acid gas species can be targeted based on injection point temperature.

Within the cement manufacturing process, the chemical composition of the downcomer dust (calcium chloride, calcium sulfate and other salts) is also important as these may block the available sites for the chemical reaction.

Injection system configuration

Two key design parameters are the reagent distribution system and the particulate control device. DSI system operations rely on the hydrated lime particles making intimate contact with the acid gas components to be removed. If the reagent distribution is not well balanced, some of the flue gas will not make contact with the hydrated lime and therefore that portion of flue gas will not have the pollutants reduced. Various tools, such as computer modelling and static mixing devices, have been effective in ensuring good gas-solid mixing. Along these same lines, a baghouse particulate collector provides added gassolid contact over an ESP and will thereby have improved performance.

Reagent properties

In general, the chemical composition of most hydrated lime reagents is very comparable. Performance difference between hydrated lime reagents is due to differences in the available surface area for reaction, as well as the particle porosity. Porosity is very important as an optimised hydrated lime product will have a large enough pore structure to prevent the reaction products from clogging the pores; yet the pores need to be small enough to avoid decreasing the available surface area for reaction.

The products

Lhoist R&D is continually working to develop and improve the company's products for specific applications. Sorbacal® SP (and Sorbacal® SPS) are examples of hydrated lime reagents that have been developed by Lhoist and engineered specifically for acid gas capture applications. Sorbacal® SP and Sorbacal® SPS have specific surface areas of >40 m²/g and pore volumes of >0.20 cm³/g, whereas good guality hydrated lime reagents produced in the US typically have a specific surface area of $18 - 20 \text{ m}^2/\text{g}$ and a porosity of ~0.07 cm³/g. It is the combined aspects of increased pore volume and surface area, coupled with an optimised particle pore distribution, that makes the Sorbacal® reagents more reactive. These physical properties provide added reaction sites and the optimised pore structure prevents the reaction products from blocking the pores and keeping the surfaces below the blockage from being able to react.

The objective

The main objective of the trial with Cemex was to determine if hydrated lime can lower HCl emissions from current uncontrolled levels to below 3 ppmvd at 7% $O_{2'}$ as outlined within the PC NESHAP regulation at one plant (Plant A). Additionally, the reagent feed rates and optimal injection location(s) were to be determined, as well as studying the benefits between Sorbacal[®] H (a standard emission control hydrate) and Lhoist's enhanced Sorbacal[®] SP.

A general layout of where the DSI system would be located within the cement manufacturing process is shown in Figure 1.

The solution

A temporary portable injection system was used during the trial activity. Two injection locations were chosen for hydrate injection, at the bypass quenching air fan and at the ID fan inlet.

Various injection rates were tested for both Sorbacal[®] H and Sorbacal[®] SP to develop the optimal feed rates for PC NESHAP regulation compliance. These trials were performed as the raw mill was out of operation in order to consider the worst case scenario for baseline acid gas emissions of HCl and SO₂.

Results of hydrated lime injection at the ID fan inlet indicated that 1000 lb/h of Sorbacal[®] H reduced the HCl at the main stack from 22 ppmv down to a compliance of 3 ppmv at 7% oxygen. Figure 2 outlines the main stack removal performance of both HCl and SO₂ while using Sorbacal[®] H.

Additionally, it was found that 50% less reagent (500 lb/h) was required when utilising Sorbacal® SP. A comparison of

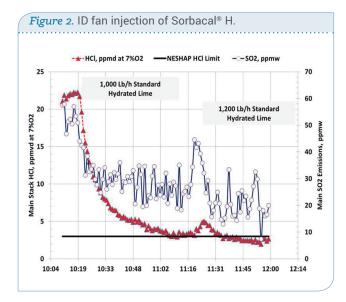
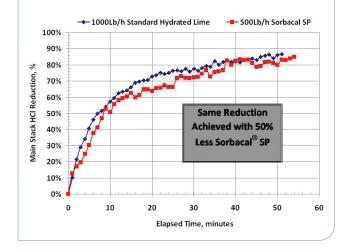
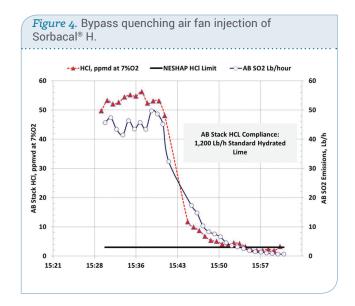


Figure 3. Comparison of Sorbacal[®] H and Sorbacal[®] SP performance for HCI removal.





reagent performance is shown in Figure 3. SO_2 emissions at the main stack were also reduced during these tests by approximately 68%.

Results of hydrated lime injection at the bypass quenching air fan indicated that approximately 1200 lb/h of Sorbacal® H was needed to reduce the HCl at the bypass stack from 56 ppmv to 3 ppmv at 7% oxygen. An existing lime slurry system on this system was set to a minimum feed rate of less than 1 gpm for the duration of these trials. SO₂ emissions at the bypass stack during these trials were also reduced by approximately 97%. These results are shown in Figure 4.

Additional testing performed at a number of other Cemex locations has shown very similar results, both in terms of HCl removal performance and the benefit of reduced reagent consumption when utilising Sorbacal[®] SP. These results are shown in Table 1.

Summary

Through a series of tests within the Cemex organisation and with collaboration from Lhoist North America, it was demonstrated that PC NESHAP regulation compliance with regard to the HCl limits can be effectively met by utilising dry sorbent injection (DSI) technology with calcium based reagents, specifically hydrated lime. All of the tests conducted to date have shown very effective acid gas removal using this technology, with removals upwards of 95%. Additionally, utilising Sorbacal® SP offers the potential for meeting these limits with much lower reagent feed rates or alternatively can achieve higher emission reductions, which standard hydrates may not be able to achieve. These reductions can be significant, not only in terms of yearly spend for reagents, but also reduced volumes of solids being generated in the waste stream that must be either disposed of or incorporated into the final product. DSI technology offers the cement industry a low capital cost and a highly effective means of treating acid gases for the PC NESHAP regulation or other regulatory drivers that plants may face. 💎

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