Reduction of Mercury Emissions from Preheater/Precalciner Cement Kiln Through the Use of Thermal Desorption of Kiln Feed

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ABSTRACT

Environmental Quality Management, Inc. (EQ) and Envirocare International have developed an innovative method of removing mercury and other pollutants from cement plant flue gases through pre-treatment of kiln feed and/or fabric filter dust prior to introduction to the kiln preheater. The process involves the indirect heating of ground meal using sensible heat in kiln flue gases and calcined meal. The evolved products are captured in activated carbon and incinerated in the kiln combustion system.

INTRODUCTION

The cement industry in the United States is regulated by the U.S. EPA under the NESHAP program through the establishment of MACT limits. EPA has proposed emission limits for mercury, THC, HCl, and particulate matter under this program. Final rules are to be issued in June 2010 and each plant will have three years to comply. As published, the rules will impact all facilities in that no single plant is expected to comply with the limits for all the pollutants without controls.

EQ and Envirocare, in anticipation of changes in the emission limits for THC, developed a thermal treatment system for removing organic hydrocarbons contained in kiln feed prior to material introduction into the preheater.

A patent was issued on October 7, 2007 pertaining to the method and operation of treating kiln feed to remove pollutants including THC, ammonia, SO_2, and other volatile species.[1] The pollutants are discharged from the treatment device in a low-volume gas stream and can be incinerated or returned to the kiln calciner for destruction. A second patent application was made in July 2008 to include the removal of mercury from the discharged gases prior to incineration of the pollutants.[2]

If mercury is to be removed from the kiln feed, the discharge stream is filtered to remove particulate matter, passed over a catalyst to convert elemental mercury to ionic form, and the mercury captured by activated carbon (which is disposed of) before the gases are returned to the kiln for incineration of other pollutants (i.e., THC, ammonia, etc.).

The advantage of the treatment system is that a small gas volume of concentrated pollutants is treated compared to the treatment of a large gas volume at system exit at low concentration when untreated kiln feed is placed in the kiln preheater.

Extensive studies at several plants have demonstrated that ionic mercury condenses on the surface of kiln feed particles at a temperature below 250°F. Because the grinding mills are used to dry the mix, which is typically 10-15% moisture, outlet gases and kiln feed are below 250°F. The mill product is stored in homogenizing silos or blend silos as a forming a surge bin for kiln feed.

When the mill is down for maintenance, the captured mercury is volatilized in the preheater and the gases are cooled to <450°F using water sprays prior to entering the fabric filter. If the gases are cooled below 250°F, mercury is condensed on the kiln recirculating dust and captured in the fabric filter. Because the recirculating dust is 5-15% of kiln feed weight, the mercury content of this dust can be 100 to 1000 times that of virgin kiln feed.

Treatment of the high-concentration filter dust is a cost-effective method of removing mercury without the additional cost of dust disposal (Table 1).

Table 1. Comparison of Mercury Content of Kiln Feed For Various Operation Scenarios

	Virgin Rock	Kiln Feed with Recirculation[a]	Recirculatory Dust[b]
Rock			
T/hr (wet)	250	231	
T/hr (dry)	210	210	
Moisture %	16.0	1.0	1.0
Temperature of Material	70.0	220	250
Hg (total ppm(dry))	0.045	4.5	49.5
Recirculatory Dust T/hr	0	21.0 [c]	21.0[c]

[a]Mill operation for 156 hrs of kiln feed capturing mercury.
[b]Mill down operation with mercury captured in recirculating dust in fabric filter.
[c]10% recirculatory load.

Physical Treatment of Kiln Feed in the Manufacturing Process

Kiln feed is the product of grinding of cement rock (mix) introduced to vertical grinding mills as part of the preheater/precalciner kiln system. The material is 95% minus 325 mesh and is combined with the recirculating dust load emitted from the top cyclone of the preheater (Figure 1). The weight of the recirculating load can be between 5 and 15% of the kiln feed depending on cyclone design and equipment age. Recirculating dust is typically 1 to 2 µm in diameter and is high in alkali salts (KCl, NaCl, Na_2SO_4, K_2SO_4).

Certain organic species such as ammonium sulfate, ammonium chloride, alkali sulfates, and alkali chlorides are retained in kiln feed during grinding and are returned to the preheater where they vaporize and/or decompose. The repeated capture and volatilization creates an enrichment cycle which is broken when the mill is taken down for maintenance. This cycle is well known and influences emission of SO_2, HCl, SO_3, NH_3, and other species.[3]

Recent studies of mercury emissions have also indicated ionic mercury species also build enrichment cycles between the preheater and grinding mill. The enrichment ratio can be as high as 2 or 15 times inlet loading depending on mix composition, chlorides, and temperature.[4]

Figure 1. Typical System

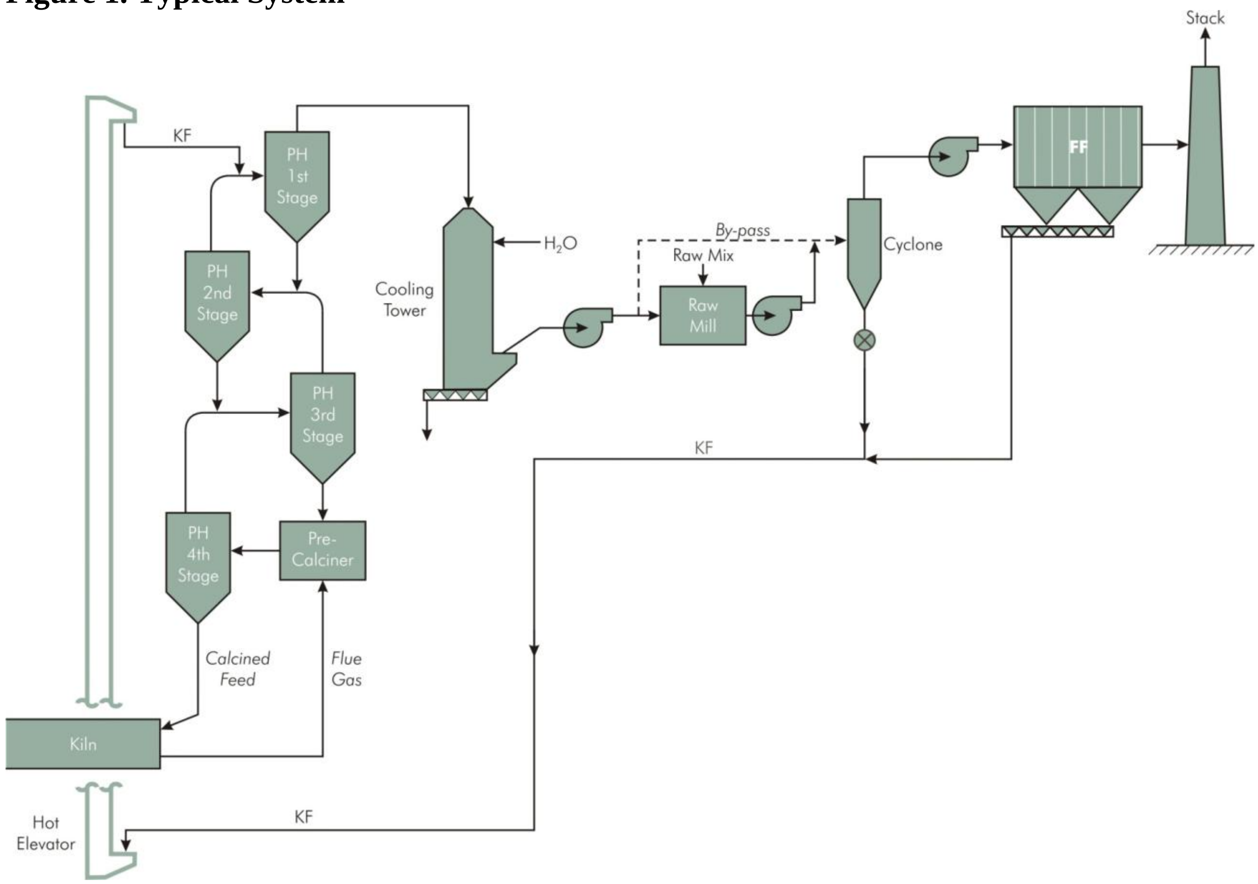


Figure 2 shows the original patent concept for removal of THC, ammonia, HCl, and sulfates. Figures 3 and 4 show the modifications added for capture of mercury in primarily ionic form and the use of SCR for conversion of elemental to ionic for capture.

Figure 2. Original Patent Concept for Removal of THC, Ammonia, HCl, and Sulfates.

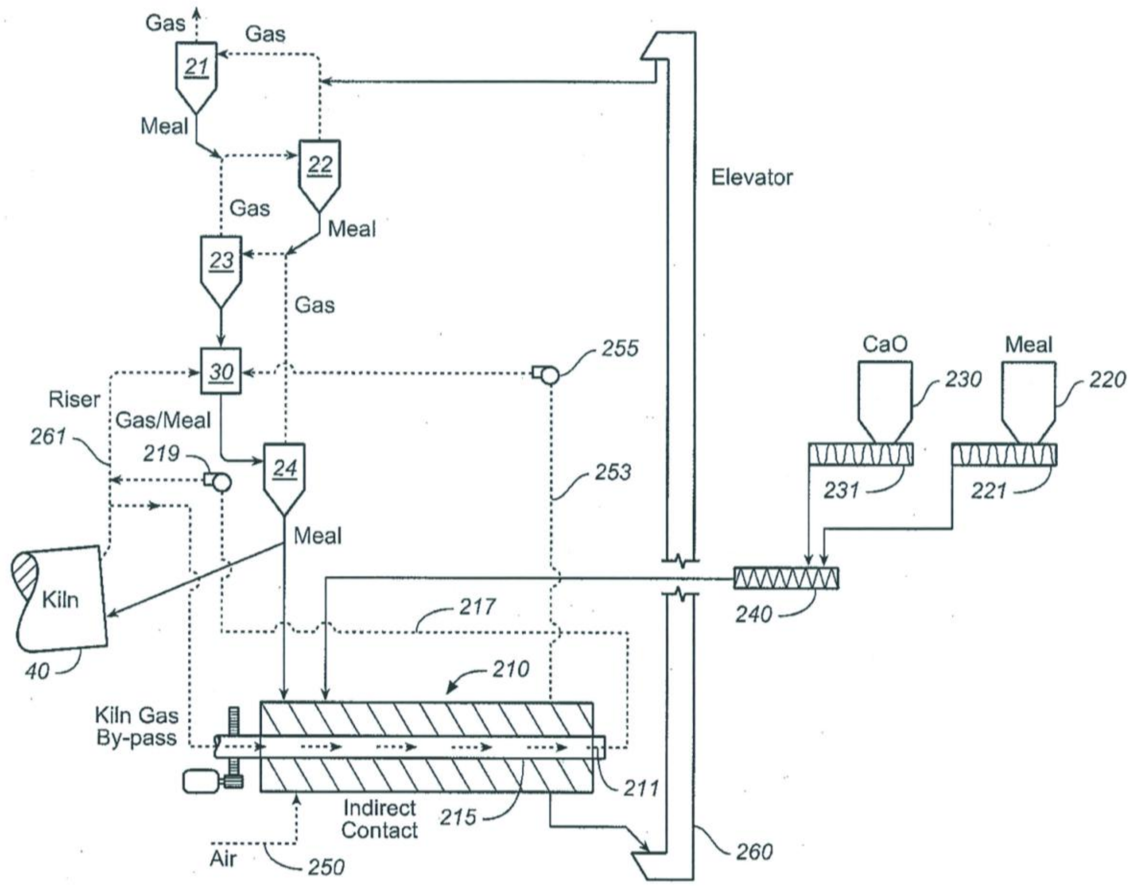


Figure 3. Modifications Added for Capture of Mercury.

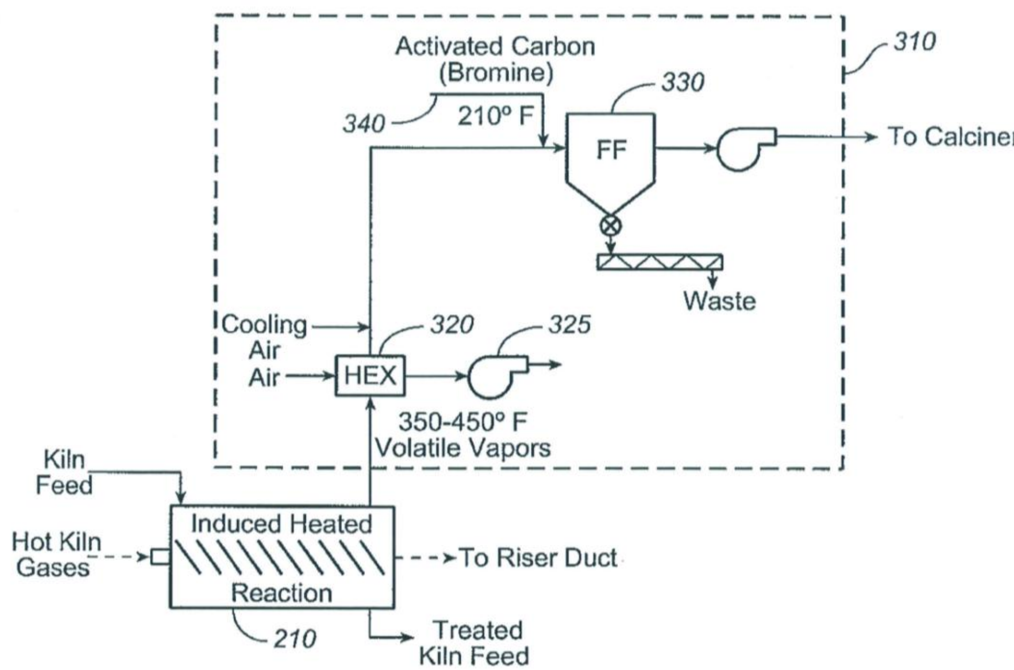
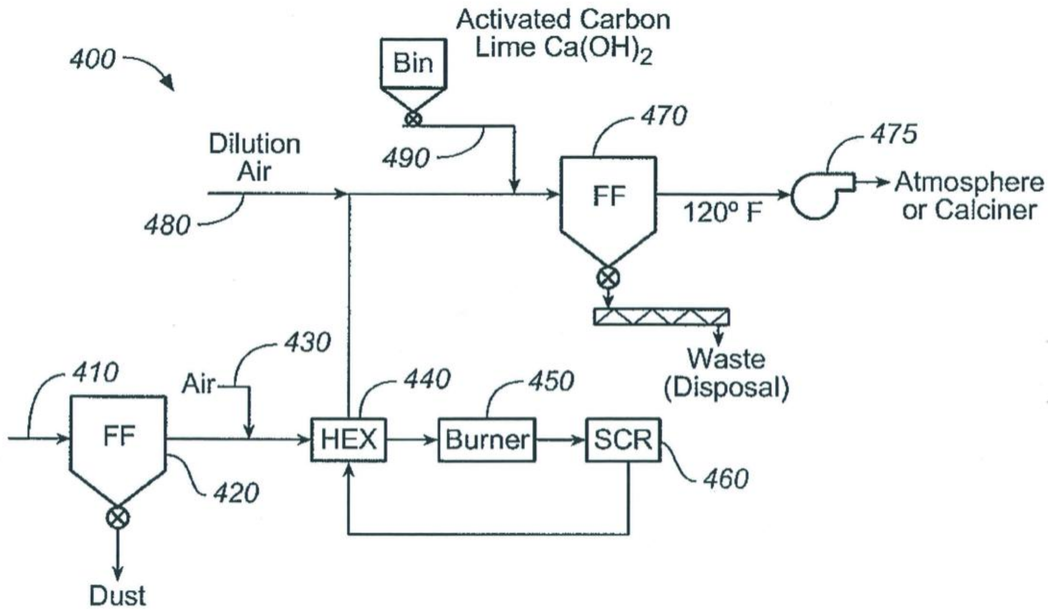


Figure 4. Use of SCR for Conversion of Elemental to Ionic For Capture.



EQ/ECI Meal Treatment System

Kiln feed and/or fabric filter dust is heated in an indirect heating process using calcined meal from the fourth stage cyclone and flue gases from the kiln riser duct (Figure 2). Calcined meal at 1500°F is mixed with kiln feed to provide direct-contact heating and to produce a basic environment for base-base exchange that allows volatile sulfur species to be removed from the dust. This also promotes the decomposition of ammonium salts which release ammonia from the enrichment cycle. Ammonia has been documented as a source of residual plumes or secondary aerosols in cement kiln systems.

Additional heating occurs through indirect contact with the flue gases via the thermal screw. The final mixture of kiln feed and calcined meal is raised to a temperature of 350° to 450°F. At this temperature, organic species such as bitumen and kerogens are vaporized and emitted into the vent gases from the reactor.

Ionic mercury species and elemental mercury in the virgin rock are vaporized and emitted with the vent gases. Vent gases are passed through a fabric filter to remove entrained dust and then through a catalyst bed in which elemental mercury is oxidized to form ionic mercury. Ionic mercury is captured on activated carbon and removed in a second fabric filter for final disposal. Gaseous pollutants such as ammonia, THC, semi-volatiles species, SO_2, and HCl are passed through the filter and injected into the calciner tertiary air system for destruction and/or incorporation into the clinker product.

The unique advantage of the system is that sensible heat removed from the process with calcined meal and flue gases is returned to the process as sensible heat of preheated kiln feed and vent gases which are returned to the process. The treatment process is almost energy neutral except for convective and radiation losses from the material transport surfaces.

Limitations of the Process

The treatment process is not a universal abatement system for MACT compliance and must be installed at those kiln systems where the amount of mercury trapped in the preheater/mill cycle is significant and the end-of-pipe treatment cost is prohibitive. It has the advantage of lower capital costs and minimal operating costs. In addition, multi-pollutant control can be accomplished in the same process unit (SO_2, NH_3, HCl, THC, etc.).

EQ and ECI have developed a pilot treatment reactor with a mobile laboratory that can be used to quantify the removal process using site-specific feed, dust, and operating conditions. This data is then used to assess if the technology is applicable for the specific kiln system.

REFERENCES

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