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RECIRCULATION OF METALS IN CEMENT KILNS

WET-PROCESS CEMENT KILNS

A primary difference between kiln designs is in the preparation of feed materials prior to calcination. In wet-process kilns, feed is prepared in the form of a slurry containing 30 to 35% water. The limestone, sand, and clay are ground with water in wet mills to produce a slurry which can be conveniently blended between slurry tanks. Blending of the slurry produces a very uniform feed and transporting wet raw mix requires less power. The penalty for using this older technology is a higher energy requirement for evaporating the water from the slurry.

In wet-process kilns, slurry is pumped into the elevated end of the kiln. The countercurrent exchange of feed materials and exhaust gas transfers heat from the gas as water evaporates and carbon dioxide is evolved. Wet-process kilns typically use many tons of chain, hung inside the kiln near the feed end, to improve heat transfer from the gas to the feed. This is commonly known as the chain zone, where exhaust gas temperatures drop from approximately 1000 °C to 250°C and where material temperatures increase from 20°C to approximately 540°C. Water and volatile organic compounds in the slurry are evaporated in the chain zone. Some semi-volatile materials which are volatilised in the burning zone tend to recondense in the chain zone.

Dust which is entrained in the exhaust gas from the kiln or chain zone is conveyed to an air pollution control device (APCD), usually either electrostatic precipitator (ESP) or baghouse. Some of this cement kiln dust (CKD) can be returned to the kiln or blended into the cement product. In wet-process kilns, all the dust picked up by the kiln exhaust gases is collected in the APCD. The dust is dry, partially calcined, and somewhat concentrated in volatile inorganic compounds. The dust cannot be directly blended into the feed because the alkalis salts tends to thicken the slurry. A few plants leach alkali chlorides and sulphates and return the leached material to the slurry. Various mechanisms are in used to return the dust but each has significant limitations. Common ways of returning dry dust are through insufflation (blowing dust into the hot end of the kiln) or through dust scoops (through holes in the kiln shell downslope from the chain section). Many kiln operators in Europe have eliminated or greatly reduced dust disposal by blending dust into clinker in finish mills.

DRY-PROCESS CEMENT KILNS

Modern cement kilns use dry-process technology which eliminates the energy penalty from evaporation of slurry water. An efficient dry-process kiln will consume only about 60 – 70% of the energy required to produce a ton of cement in a typical wet-process kiln. However, raw grinding and homogenisation of the feed materials is more difficult and the design of the modern preheater kiln is more complicated, resulting in increased process-control challenges and increased electric power consumption.

Long dry kilns

Dry-process kilns of the simplest type are known as long dry kilns. They are very similar to wet-process kilns utilising chains at the feed end for heat transfer and very long kiln lengths to calcine and prepare the feed. Driving carbon dioxide from limestone (calcining) requires a great deal of the fuel energy. However, this process takes place at relatively low temperatures from 550 to 900°C. Releasing some of the carbon dioxide before the feed enters the rotary kiln makes it possible to achieve much higher production for a smaller size kiln.

In long dry-process kilns, as in wet kilns, all the dust entrained in the kiln exhaust gases is collected in a dust collector, usually a baghouse or ESP. Many dry-process kilns utilise cyclones to capture 70 – 80% of CKD as it leaves the kiln, but prior to entering the final dust collector. The CKD resembles raw mix with an elevated concentration in volatile inorganic compounds. Dust can be recycled to the kiln, blended into cement, or disposed depending on chemical constraints of a specific plant and the specifications for the product being produced. If any dust is disposed, the purpose is to purge the product of excess sulphur, alkalis (potassium and sodium), or chlorine which would adversely affect the cement quality.

The kiln exit dust in long dry kilns with cogenerating boilers is typically a highly calcined product concentrated in volatile elements. CKD is collected in this type of kiln by at the boiler, cyclones, or the main APCD. In practice, the main APCD dust and part of the other streams is removed from the kiln to reduce volatile compounds in the kiln system.

Preheater/Precalciner kilns

Modern dry-process kilns use a suspension preheater or a Lepol grate preheater system to prepare and partially calcine the feed before it enters the rotary kiln. A further advancement in cement kiln technology is the preheater/precalciner kiln, where fuels are combusted in the preheater system just upstream of the rotary kiln. Low grade fuels, which have a much higher ash content, can be used in a precalciner kiln because the temperatures required for calcination are much lower than the temperatures needed to fuse the minerals into clinker. Approximately 30 to 60% of the kiln fuel may be burned in the precalciner to release up to 90% of the carbon dioxide of the raw mix prior to entering the kiln. This type of process is thermally efficient because heat is added where it is needed. For the same reason, mid-kiln injection of tyres or other wastes can provide significant energy improvements in addition to mechanical improvements (smaller kilns, etc.) by releasing the energy where calcination is occurring.

In preheater/precalciner kilns with bypasses, CKD from the main exhaust gas stream is usually returned to the raw feed. Significant amounts of volatile inorganic compounds can be diverted through the bypass system. The bypass in preheater/precalciner kilns consists of a duct which extracts a slip stream of gas out of the kiln gases after they exit the kiln and before they go into the preheater. This gas stream is extracted to remove volatilised minerals from the kiln and thereby control the level of these minerals in the kiln system. The bypass gas is cooled, the particulates are condensed and collected, and the gas is cleaned and exhausted to the atmosphere. Thus, there are two exit gas streams from the process. One at the main stack after the preheater/precalciner and the other at the bypass via a separate collector.

The bypass gas stream is much smaller than the main stack gas. The dust collected in the bypass APCD is highly concentrated in volatile compounds, and is usually removed from the kiln system. In multi-stage preheater/precalciner kilns without bypasses, the dust collected in the main dust collector is very similar to raw meal. A bypass allows kilns with raw materials containing high concentrations of alkalis to minimise the amount of dust that is disposed. As with wet-process kilns, some or all of the dust collected from the bypass may be blended into the cement in the finish mills.

VOLATILISATION AND CONDENSATION

Materials ordinarily considered non-volatile will melt and vaporise at the extremely high temperatures in the burning zone of a cement kiln. This is illustrated by following melting and boiling points for materials of interest:

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Substance	**Melting Point °C**	**Boiling Point, °C**
Potassium chloride (KC1)	790	1413
Sodium chloride (NaC1)	801	1407
Sodium sulphate NA_2SO_4)	884	1499
Lead oxide (PbO)	888	1472

Sodium and potassium combine with sulphates and chlorides in the burning zone of the kiln. These salts then volatilise near the boiling point temperatures listed above. Similarly, lead compounds introduced with the feed or fuel are volatilised in the burning zone and carried with gases to cooler regions of the kiln.

The kiln gases remain above 1000°C for typically 3 to 6 seconds in most cement kilns. The gases cool as the heat is transferred to the feed material. Exhaust gases are typically at temperatures between 105°C and 350°C as they exit the kiln stack. Consequently, potassium chloride, lead oxide, or other materials volatilised in the burning zone tend to condense onto particle surfaces. Materials that volatilise in the burning zone and condense downstream generally become fume particles smaller than 0.1µm in size. These particles exhibit Brownian motion and rapidly collide with other particles, combining to form particles 0.1 to 1.0µm in size. Material volatilised in the burning zone tends to accumulate on surfaces of small particles of feed material in cooler areas of the kiln. As the feed material, which has trapped volatilised salts, moves into hotter regions of the kiln, the volatile components once again evaporate and recirculate within the kiln system. Enrichment of alkali chlorides or sulphates and other volatile materials occurs in the kiln materials as a result of this process. Some dust containing these alkali chlorides and sulphates may have to be removed from the kiln system to prevent operational problems such as excessive fluxing, ring formation in kilns, or plugging of preheaters/precalciners. Most cement plants in Europe blend all or part of dust into cement when clinker is ground. This is not done in the United States because it is specifically excluded by ASTM standards.

REMOVAL OF CKD FROM KILN SYSTEMS

The nature of clinker and CKD can be significantly affected by the design, operation, and materials used in a cement kiln. For any cement plant operation, there is a limit as to how much sulphur, alkali, or chlorine the system can tolerate. Excesses must be removed by removing kiln dust. The determining factor for the amount of dust which must be removed is known as the "driver" since its concentration in the raw materials, fuels, and clinker is what dictates or drives the dust removal rate. In many cases, most or all of the dust can be reintroduced into cement when clinker is ground with gypsum. However, there is a limit to how much sulphur, alkali and chlorine can be in cement without adversely affecting quality. In extreme cases some dust must be wasted.

The major parameters which influence the CKD generation rate from a kiln are the following:

- input of sulphur, potassium, sodium, and chlorine from fuels and raw material;
- volatilisation rates in the burning zone;
- condensation profile through the various stages of dust collection, and
- concentration of the driver element in the CKD.

ALKALIS AS THE DRIVER

Some cement plants use raw materials which contribute higher inputs of alkalis than can be accepted in the clinker. For some markets, alkali content of the clinker has to be limited to meet local product specifications. Alkalis can also change the melting point of clinker material causing kiln instability. Consequently the kiln dust, which has a higher concentration in alkalis than the raw meal, is removed to reduce the alkali content of the clinker or improve kiln stability. In these plants, alkalis are the driver. Introduction of additional sulphur or chlorine to these systems will not necessarily change the dust wasting rate.

SULPHUR AS THE DRIVER

Dust wasting at most cement plants is strongly influenced by sulphur introduced with the raw materials and the fuel. Sulphur compounds are volatile at the temperatures found in the burning zone. They vaporise and travel with the exhaust gases to a zone where the temperature is low enough for them to condense. They then return with the kiln dust, building up in the material charge in the kiln. The material charge typically has concentrations of sulphur about three to eight times that found in the clinker. At elevated concentrations of sulphur, the kiln charge material causes formation of blockages or leads to unstable kiln operation. To avoid this, the operators remove some kiln exit dust in order to purge sulphur from the kiln. The amount of sulphur which can be trapped in the clinker depends on the burning zone atmosphere and temperature and also on the alkali desired content of the clinker. Any sulphur which is not trapped in the clinker and which does not escape in the form of sulphur dioxide emissions, must be removed by removing dust. In this case, sulphur is the driver. Introduction of additional alkalis or chlorine to a sulphur-driven system will not necessarily change the dust wasting rate.

CHLORINE AS THE DRIVER

Chlorine compounds are highly volatile at the temperatures found in the burning zone. They vaporise and travel with the exhaust gases to a zone where the temperature is low enough for them to condense. They then return with the kiln dust, building up in the material charge in the kiln. The material charge typically has concentrations of chlorine 100 times that found in the clinker. At elevated concentrations of chlorine, the kiln charge material causes formation of blockages and leads to unstable kiln operation. To avoid this, operators remove some kiln exit dust in order to purge chlorine from the system. The amount of chlorine which can be trapped in the clinker is very small, typically less than 1000 ppm. Both raw materials and fuels can contribute chlorine to the process. In the absence of other drivers for dust wasting, chlorine can be the driver at input levels as low as 0.025% by weight of clinker. Introduction of additional sulphur or alkalis to these systems will not necessarily change the dust wasting rate.

OPERATIONAL LIMITATIONS AS THE DRIVER

In certain cases mechanical limitations make it difficult to convey and meter dust back to the kiln process. This is often the case for wet-process kilns. The dry, partially calcined dust cannot be returned to the feed end, or mixed with the feed slurry, as this causes the slurry to thicken or “gel” leading to unstable kiln operation. Some wet process plants have equipment to insufflate dust by pneumatically conveying it into the burning zone of the kiln. The amount of dust which can be returned this way is usually less than the amount collected in the main dust collector. Insufflation also increases the amount of dust which must be removed from kiln exhaust by the APCD. This can cause an increase in kiln stack emissions and difficulty maintaining compliance with air emission standards.

The type of APCD can also be a physical driver. Small particles of condensed sulphates and chlorides are not captured in the first stages of an ESP and tend to concentrate in the later stages. This allows operators to remove a small amount of highly concentrated dust. This concentrating effect is not possible with baghouses and therefore, more dust must be removed to remove the same amount of sulphates and chlorides.

Preheater kilns which are not equipped with a bypass are severely limited with respect to alkalis, chlorides and sulphur tolerance because volatilised alkali chlorides re-circulate and accumulate when not removed. Accumulation of sulphates or chlorides causes the feed to become sticky and plug preheater cyclones. For many kilns of this type, the main dust collector serves both the kiln and the raw mill. Therefore, dust is not as concentrated in volatile compounds because the kiln dust is diluted with dust from the mill. This puts tight specifications on the feed materials. It may be necessary to remove a large amount of dust from the kiln system if the raw materials or fuels are relatively high in sulphur, alkalis or chlorine. Kilns of this type are only practical when the dust can be blended into the cement product or where the raw materials and fuels permit operation without disposing of large amounts of dust.

Perhaps the easiest way to understand how the operation and design of a kiln can affect CKD and clinker is to consider intermittent operation of an alkali bypass system for a modern precalciner kiln. The kiln system may be operated with the alkali bypass system totally closed and no CKD generated. This causes alkali sulphates and chlorides, as well as other volatile metal salts, to accumulate in materials re-circulating within the kiln. If the alkali salts accumulate beyond approximately 1 to 2% in material in the preheater cyclone, plugging and other operating problems will occur. Intermittent operation of the alkali bypass is used to flush out accumulated salts. Consequently, dust generated intermittently typically has much higher levels of alkali and volatile metal salts than dust generated continuously in this type of system.

THE EFFECT OF RAW MATERIALS AND FUELS

Most raw materials contain compounds of sulphur, alkalis, and chlorine. Raw materials in Europe are frequently lower in sulphur and alkali compounds than those used by cement manufacturers in North America. This, along with the ASTM prohibition on blending dust into the product, results in considerably more dust being wasted in North America.

All fuels, contain compounds of sulphur, alkalis, and chlorine. Petroleum coke, heavy oil, and some coals typically have 1 – 5% sulphur and less than 1% chlorine. Blended waste fuels often have 1 – 3% chlorine and less than 1% sulphur. Concerns about alkalis are usually related to the raw materials and rarely a concern with fuels.

Fuels and raw materials together make up the total input to the system of sulphur, alkalis, and chlorine. Any excess input of the driver element beyond what is combined into the clinker is removed either through gaseous emissions (for example as sulphur dioxide) or with the waste dust (for example as calcium sulphate, alkali sulphate, or alkali chloride salts).

In certain cases, it is advantageous to use fuels which contain chlorine in preference to those with large amounts of sulphur. The chlorine will tend to combine with the alkalis to form alkali chlorides, which are more volatile and thus easier to concentrate in the waste dust than are the alkali sulphates. Use of chlorine-containing fuels can lead to a reduction in dust wasting for plants supplying markets with low-alkali cement or that have excess alkalis in their raw materials. In this case, chlorine helps to remove alkalis, improving product quality and reducing the amount of dust disposed. Similarly, dust wasting can be limited by substituting low sulphur-containing fuels in plants where sulphur is the driver.

For the most part, operators of kilns which do not dispose of dust have found that it is not economically interesting to begin burning waste fuels, except at very low chlorine input levels, since to remove the chlorine they would have to start wasting dust. This change in operation would require considerable capital costs for the installation of a dust wasting system and may result in lost clinker production.

As a further example of the effect of changes in raw materials and fuels, consider a raw material source that contains other metals, for example lead, a relatively common element in the earth's crust. The source, a required feed stock, may be naturally occurring iron ore or limestone, a component derived from an inert industrial by-product; or possibly a hazardous waste. Volatile metals, like lead, increase considerably in the kiln materials if not removed by removing dust from the kiln. In fact, the lead level may be much higher in this type of kiln than in another kiln which uses lead-bearing waste derived fuels and wastes CKD.

Use of industrial wastes and by-products should not automatically be rejected as a sources of raw materials and fuels because they contain volatile or semi volatile materials. The overall picture may well be that it is economically and environmentally beneficial to promote resource conservation and waste minimisation while producing an essential product, cement. A wealth of information is available for understanding the fate of materials in cement kilns. It should be used, along with appropriately designed monitoring programs, to make decisions that are the best practical environmental option.