# REDUCING PREHYDRATION

**Jeffrey Thomas and Joshua Detellis, GCP Applied Technologies,** explain the use of grinding aids in vertical roller mills to reduce cement prehydration.


## Abstract

Vertical roller mills (VRMs) have important advantages over ball mills for the production of cement, including greater energy efficiency, smaller plant footprint, and the versatility to grind multiple cement types under different conditions. However, cement produced in VRMs sometimes exhibits lower strengths and longer initial setting times compared to ball-milled cements made with the same raw materials. This degradation in properties can be directly linked to prehydration of the cement, which is caused by the presence of moisture inside the VRM. A primary source of moisture is the spraying of water onto the clinker as it is ground, which is routinely done to stabilise the layer of clinker that passes under the rollers, known as the grinding bed. Fortunately, the need to spray water can be reduced significantly through the use of suitable grinding aids that stabilise the grinding bed without causing prehydration. This paper presents data from VRM field trials that directly correlates VRM water spraying levels to prehydration of the resulting cement and then further links this prehydration to lower strengths and longer setting times. These findings demonstrate how reducing the prehydration of a VRM operation has the potential to significantly improve the resulting cement performance.


## Introduction

Since VRMs were introduced in the 1990s as an alternative to ball mills for finish grinding of cement, they have gained an increasing footprint in the market. In a VRM, the particles are ground by a combination of compressive and shear forces as a roller passes over a compacted bed of material. This is quite different from a ball mill, where grinding occurs by dynamic impacts. As a result, operation of a VRM is more energy efficient, with less energy lost to heat and sound. Production of cement in a VRM is estimated to be about 36% more efficient than production in a ball mill, on the basis of tonnes of finished cement produced, which leads to direct cost savings. In addition, VRMs have other advantages, such as a relatively small footprint and short residence times, which allow for rapid adjustments to the grinding operation.

Despite these advantages, it is often observed by plant operators that the strength and setting times of the cement produced in a VRM is inferior to that produced from the same raw materials in a ball mill. In the past, this was often blamed on insufficient gypsum dehydration in the VRM. However, it is now clear that, in the majority of these cases, the cause of the problem is prehydration of the cement, which can be broadly defined as an unwanted reaction between cement and water that occurs before the final intended use of the cement. It has long been known that prehydration has a negative effect on cement properties and that the magnitude of these negative effects increases as the amount of prehydration increases.[1] These negative effects include the following:

- Reduction of compressive strengths at all ages, with the greatest reductions at early ages.
- Delayed mortar and concrete setting times.
- Reduced bulk powder handling properties, such as flowability, lump formation, and blockage.
- Reduced mortar and concrete slump.
- Inconsistent chemical additive and admixture performance

In both VRMs and ball mills, water may be sprayed onto the material as it is ground, resulting in prehydration of the cement that is produced. However, VRMs tend to use considerably more water than ball mills; thus cement produced in VRMs exhibits, on average, higher prehydration levels than cement produced in ball mills. GCP Applied Technologies recently conducted a survey of 181 different cements produced in both ball mills and VRMs.[2] The survey found that 48% of the VRM-produced cements had a problematic level of prehydration, versus only 19% for ball mill-produced cement.

## Prehydration mechanisms and morphology

While prehydration is a reaction between cement and water, it differs in important ways from normal hydration. In the normal hydration process, the cement particles are surrounded by liquid water, resulting in extensive dissolution of the cement minerals and allowing the hydration products to grow out away from the particle surfaces. With prehydration, the water is generally present as a vapour that adsorbs in limited quantities onto the cement surface. Under these conditions, only the most soluble phases tend to dissolve and react. In cement, these are generally the free lime (CaO), the alkali sulfate phases, and aluminate phases.

Importantly, due to the limited availability of water, prehydration products tend to form as a compact layer around the cement particles (Figure 1). This layer tends to limit the further dissolution of the cement particles, delaying setting and strength development. The presence of the layer can also interfere with the action of chemical additives, rendering them less effective. Thus, it may be difficult to mitigate the effects of prehydration by using accelerators or traditional quality-improving grinding aids. The common adjustment made by plants in response to prehydration is to grind the cement to a higher fineness. This has well-known disadvantages, however, such as increased energy consumption, decreased throughput, and increased water demand for the finished cement. In summary, the prehydration of only a small fraction of the cement during finish grinding can have quite significant effects on the properties of the cement when it is used to make concrete or mortar. Mitigating these effects after the prehydration has occurred can be difficult.

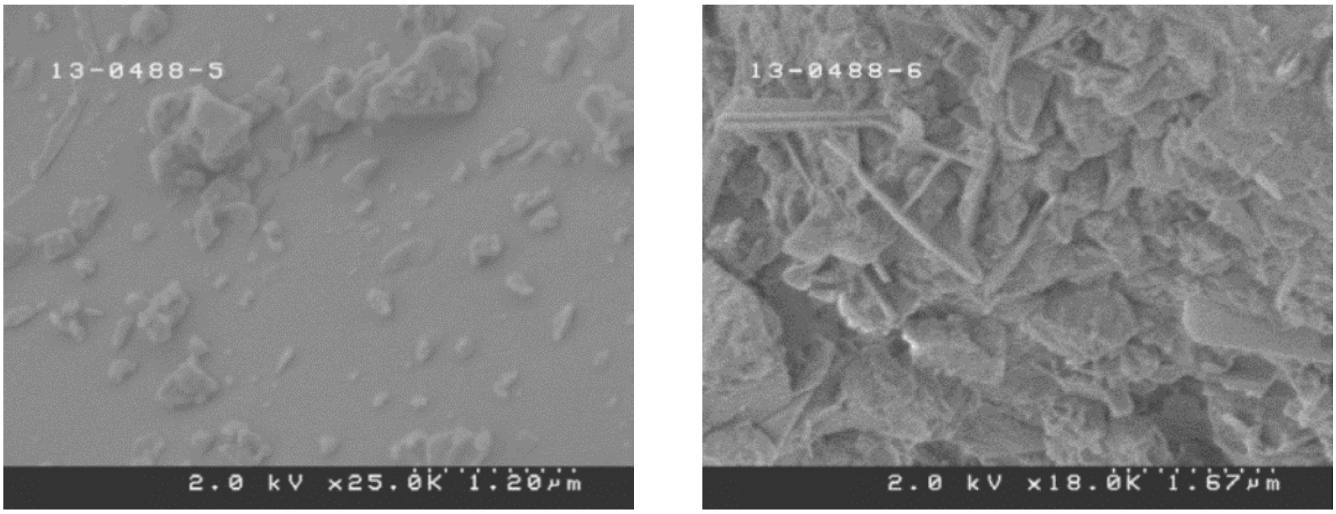


Figure 1.Scanning electron microscopy (SEM) images of two cement particles. Left: cement with minor prehydration – the cement surface is mostly smooth and free of hydration products. Right: cement with severe prehydration – the surface is completely covered with a dense layer of hydration products that will act as a barrier, reducing the reactivity of the cement when mixed with water.

### Causes and mitigation of VRM prehydration

There are a number of factors that make VRMs more susceptible to causing cement prehydration compared to ball mills. Probably the most important of these is the practice of spraying water onto the grinding bed of a VRM in order to stabilise the bed and reduce mechanical vibrations, which can cause damage to the equipment. This continuous introduction of moisture into the mill is certainly a major factor in prehydrating cement. Other factors include recirculation of moist process gasses, which is done to keep the VRM outlet temperature up and limit the use of external heating, and lower operating temperatures, which can limit evaporation and increase the relative humidity compared to a ball mill.

Another issue that is related to prehydration is silo set, which can occur when cement undergoes gypsum dehydration followed by additional prehydration after being stored in the silo. In a VRM, low operating temperatures, high humidity levels, and short residence times often result in minimal gypsum dehydration. Therefore, VRM outlet temperatures should generally be maintained at a low enough level such that the cement is not above about 70°C when it enters the silo. A good recent discussion of VRMs and silo set is given by Canut and Theisen.[3]

There are two broad strategies for reducing prehydration in a VRM. The first strategy is to reduce the amount of water sprayed onto the VRM table through the use of a grinding aid that stabilises the grinding bed. This is discussed in more detail below. The second strategy is to perform various operational adjustments to the mill. While VRM operation is quite complex and there are a number of factors and strategies that can be effective, the primary goal is to increase the amount of moisture that is removed from the mill in the exhaust gas stream. This typically entails increasing the amount of fresh, relatively dry air brought into the mill, while reducing the recirculation of moisture-laden process gasses.[4]

At some plants that manufacture blended cements, a significant amount of water may be introduced into the VRM in the raw feed. Natural pozzolans appear to have the greatest capacity for bringing in moisture, but limestone and even gypsum may also have appreciable moisture. In terms of prehydration, the total water introduced by spraying and in the raw feed is what matters.

In general, both strategies (use of a grinding aid and process adjustments) can be implemented for best results. Their benefits are demonstrated by the results of two field trials discussed later in this paper.

### VRM grinding aids to reduce vibrations

The smooth operation of a VRM is highly dependent on the characteristics of the grinding bed, which is defined as the layer of material on top of the grinding table. The VRM rollers pass over the grinding bed, compressing it and causing particle fracture. It should be noted that the material on the grinding bed consists not only of the relatively coarse raw material that has just entered the mill, but also partially ground material that is much finer, but has not yet passed through the separator. Factors that affect the quality of the grinding bed include the material quantity (and bed height), particle size distribution, bulk mass flow, and compressibility. Of particular importance is the amount of very fine material in the bed. The presence of fines has a negative effect on grinding: it is believed that the fine particles distribute the compressive forces in the grinding bed in such a way that less particle fracturing occurs, making the grinding process less efficient.

As noted above, water is typically sprayed onto the VRM bed. This water causes the finest particles to agglomerate, which effectively makes them behave more like large particles in terms of the behaviour of the bed. This practice is quite effective at reducing mill vibrations and allowing for stable VRM operation; however, spraying water onto the bed causes cement prehydration. The more water sprayed the higher the degree of prehydration.

A more effective way to stabilise the grinding bed is by the use of a process grinding aid applied either directly to the grinding bed or to the raw feed as it enters the VRM. The use of a grinding aid to stabilise the bed allows the water spray to be reduced, and may also allow the production rate to be increased.[5] Grinding aids are believed to stabilise the bed by dispersing the fine particles so that they do not stick to the larger particles or to each other. As a result, they pass more readily through the separator and into the cement product, so fewer fines are returned to the grinding bed. As a result, the bed is more stable and the grinding process is more efficient.

In general, grinding aids for ball mills tend to also provide benefits for VRMs.[5] In particular, the dispersing effect tends to benefit both types of systems. However, the operation of a VRM is quite different from that of a ball mill in many respects, so it is not surprising that grinding aids formulated for ball mills are not optimal for VRMs. GCP Applied Technologies has used its extensive experience with both types of grinding systems to develop a new product line of grinding aids that are specifically formulated for VRMs, known as TAVERO™ VM grinding aids.

## Experimental methods

### Measuring prehydration

Prehydration is measured by heating a cement sample and measuring the weight loss within a defined temperature range. As originally defined by Thiesen and Johansen, prehydration was quantified as the parameter Wk, which is the percentage mass loss of a sample as it is heated to just before the portlandite starts to decompose (about 375°C), but adjusted to remove the contribution to the mass loss from gypsum and plaster dehydration.[1] Prehydration is

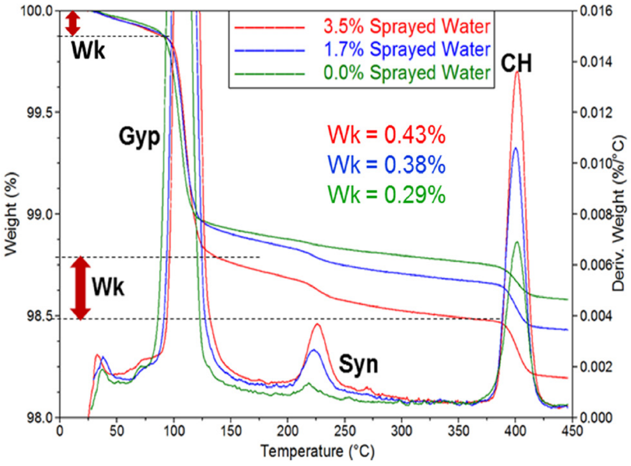


Figure 2. Thermogravimetric analysis of three cements produced in a VRM with different amounts of water spray. The peaks in the differential weight loss curves represent decomposition of specific phases: GYP-gypsum and plaster, SYN-syngenite, and CH-portlandite. Wk is the percent mass loss up to the start of portlandite decomposition, excluding the gypsum dehydration. From the cumulative curves, it can be seen that Wk increases as the sprayed water increases. The Wk value for the 3.5% water sample is the sum of the two regions at left labelled "Wk".

most accurately measured using a thermogravimetric analysis (TGA) instrument. Figure 2 shows TGA data for three VRM-produced cements with varying degrees of water spray, and therefore varying levels of prehydration. Shown are both the derivative curve (rate of mass loss vs. temperature) and the cumulative curve (mass vs. temperature). It should be noted that other temperature ranges could be used to measure prehydration; for example, the small weight loss before gypsum dehydration may be excluded.[2] Naturally, the resulting values will be different, but the trends obtained should be similar.

## Sample collection and testing

Results reported here were measured using samples collected during field trials conducted at two VRM plants. After adjusting the operating parameters of the VRM, such as feed rate, additive dosage, and water spray rate, to the desired levels, the VRM was run for at least 30 min. to ensure stable operation and that the cement being produced represented the current conditions. Approximately 3 kg of cement was collected from the output belt and, once cooled to near room temperature, the cement was vacuum-sealed in plastic bags using a small vacuum sealer. The samples remained sealed until the time of measurement. All reported

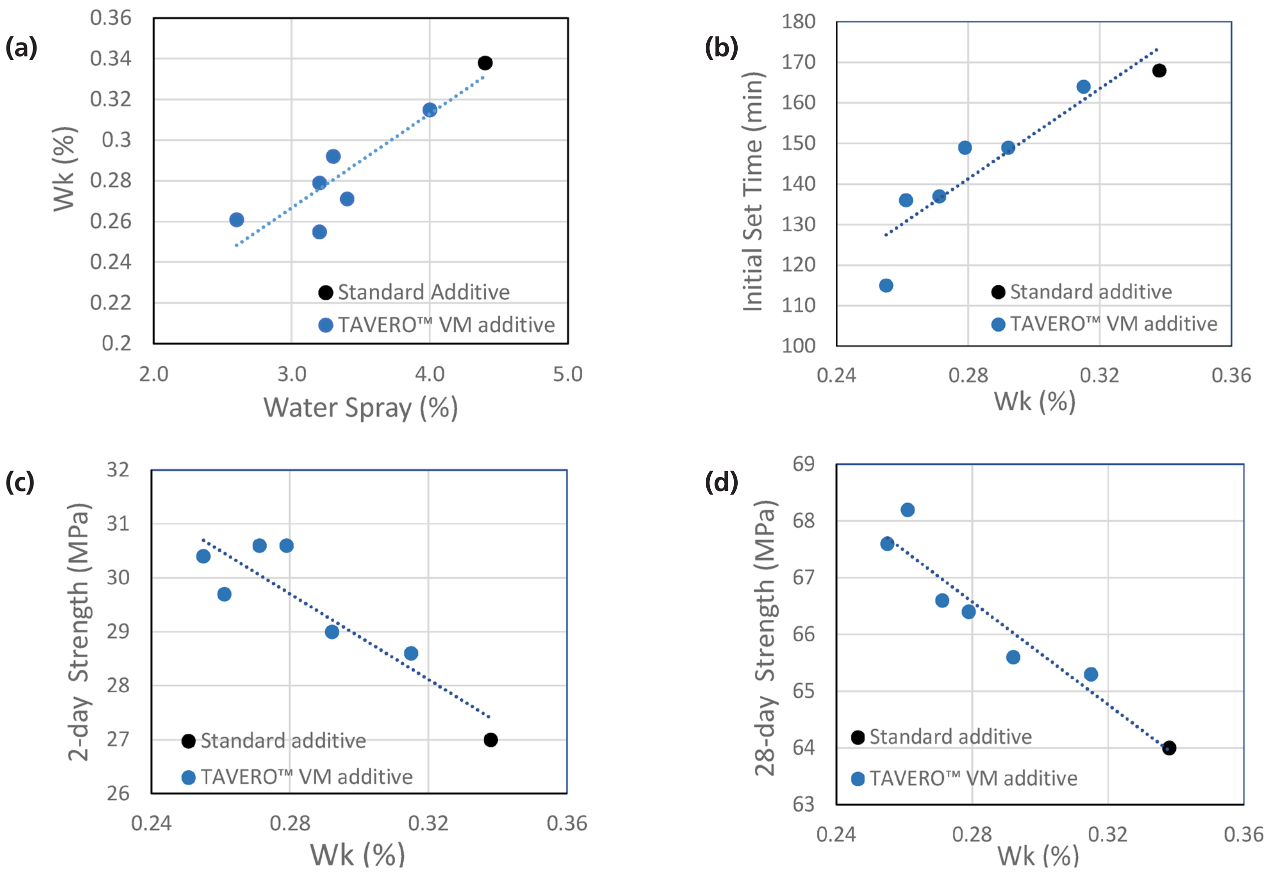


Figure 3. Results from VRM field trial 1, illustrating the improvements in cement quality that can be obtained by reducing prehydration (Wk). a) Prehydration of cement samples, plotted as a function of the water spray level. b) Initial setting time, plotted as a function of prehydration level. Mortar compressive strengths at two-days (c) and at 28 days (d) plotted as a function of prehydration level.

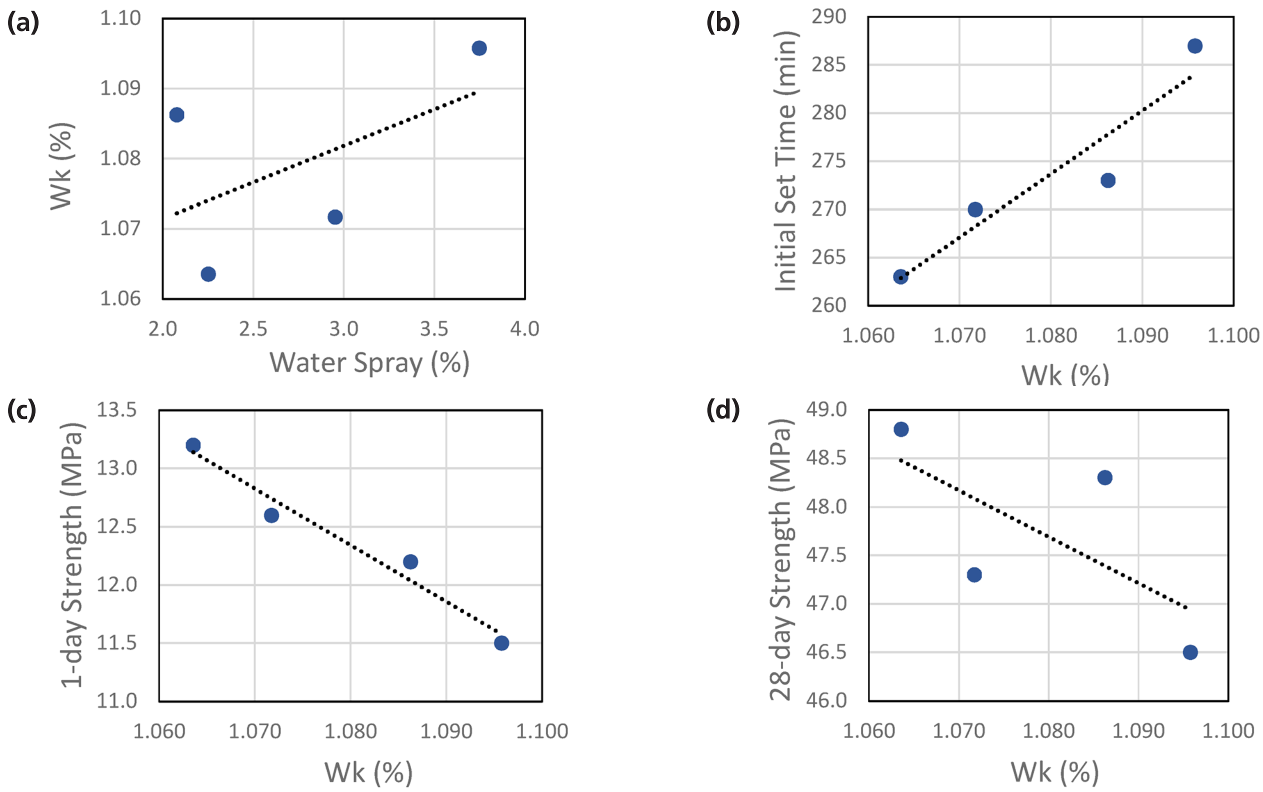


Figure 4. Results from VRM field trial 2, illustrating the improvements in cement quality that can be obtained by reducing prehydration (Wk). a) Prehydration of cement samples, plotted as a function of the water spray level. b) Initial setting time, plotted as a function of prehydration level. Mortar compressive strengths at 1-day (c) and at 28-days (d), plotted as a function of prehydration level.

compressive strength and setting time results were measured following EN 196-1 and EN 196-3 testing standards, respectively.

## Results

### Field trial 1

The first case study is a field trial at a VRM plant manufacturing a Type I cement, consisting of 90% clinker, 5% limestone, and 5% gypsum. The moisture content in the raw feed was minimal. Cement production rate was 176 tph at the start of the trial, but increased to just over 200 tph by the end of the trial. Water spray onto the grinding table was 4.4 % by weight of raw feed at the start of the trial with the use of the plant's traditional ball mill grinding aid. The mill outlet temperature was maintained at 85°C.

After replacing the plant's current grinding aid with a TAVERO™ VM grinding aid, the water spray was progressively reduced to 2.6%, while also making other process adjustments to the mill. Cement samples were collected and sealed for later analysis during this process. Figure 3(a) shows the prehydration of the cement as a function of the total water input (expressed as a percentage by mass of the raw feed). It was possible in this trial to decrease the prehydration level (Wk) by 0.08%, when water spray was reduced from 4.4 to 2.6%. As shown in Figure 3, this decrease in prehydration resulted in strength increases of approximately 3.5 MPa at both 2 days and 28 days, as well as a decrease in initial setting time of about 45 min. These are significant performance improvements, given the relatively modest change in prehydration.

### Field trial 2

The second case study is a field trial conducted at a plant manufacturing a blended cement containing 74% clinker, 22% natural pozzolan, and 4% gypsum. Production rate was 87 tph. In this case, there was a high raw moisture content of the pozzolan of 10%, resulting in about 2 tph of water being introduced into the VRM from the raw feed. Water spray onto the grinding table was 3.6 tph at the start of the trial. The total initial water input was thus about 6.4% by mass of feed, which is almost 50% higher than for Case 1. The mill outlet temperature was 87°C.

After starting the application of a TAVERO™ VM grinding aid, the water spray onto the table was reduced from 3.7 to 2.1%. Figure 4 shows the relationships between water spray, prehydration, and cement properties. Notably the measured Wk values are roughly three times the values measured in Case 1. This is mostly due to the water content and Wk contribution of the pozzolan. Despite the high level of prehydration, the benefits of reducing the prehydration by 0.04% helped improve set time by 20 min. and 1 and 28 day strength by 1.7 and 2.3 MPa, respectively. Interestingly, the cement with the lowest water spray had the second highest Wk value but, as seen in the figure, the setting time and the compressive strength of the cement samples follow the measured Wk values. This indicates that water spray is not the only factor for prehydrating the cement. If the pozzolan being added to the mill has a range of moisture contents, this could cause a cement sample taken with low water spray to still exhibit a high level of prehydration.

## Conclusions

Cement produced from VRMs are much more likely to suffer from prehydration compared to cement produced from conventional ball mills. This is due primarily to the additional water spray used to stabilise the VRM grinding bed. A prehydrated cement will have deteriorated properties, such as lower compressive strength and longer setting time. In order to reduce water spray in a VRM, grinding aids can be used to help stabilise the grinding bed. In the two field trials discussed here, replacement of a standard grinding aid with a grinding aid optimised for VRM grinding have been demonstrated to allow for a substantial reduction in water spray, with corresponding decreases in prehydration level. As a result, compressive strengths were increased by up to 5 MPa and initial setting time was decreased up to 45 min

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## About the authors


Jeffrey Thomas is a Senior Principal Scientist at GCP Applied Technologies in Cambridge, Massachusetts, US. Previously, he was a Principal Scientist with Schlumberger and a Research Professor at Northwestern University. He has authored more than 70 scientific articles in the area of cement chemistry.

Joshua Detellis is a Chemist at GCP Applied Technologies in Cambridge, Massachusetts, US. He received his master's degree in Chemical Engineering from the University of Massachusetts. He has 7 years of experience working in the cement industry.