Monitoring the rutile/anatase ratio in TiO_2 production

Benefits at a glance

- Rapid, on-line data acquisition for real-time process control
- Fiber optic coupling allows remote sampling to prevent damage to the instrument by TiO_2 dust
- Monitoring of high-temperature, abrasive materials
- Feedback control of the reactor

Introduction

Titanium dioxide (TiO_2) is the whitening additive of choice in myriad commercial white products, including toothpaste, paper, fabrics, plastics and paint, to name just a few. When prepared as a powder of microscopic crystals, TiO_2 is an excellent whitener because the size and high refractive index of these crystals ensures that visible light is efficiently scattered. It offers a wide dynamic range, and delivers the required sensitivity, down to 100 ppm for key components.

Reaction summary

Worldwide annual production presently totals millions of tons. A significant fraction of this TiO_2 is produced using the rotary kiln process. A kiln reactor is essentially a large (approximately 60 m long x 5 m diameter), slowly rotating cylinder supported at a slight incline. A high-power gas flame burner is mounted inside the lower end of the furnace. This creates a thermal gradient that peaks at the lower end of the furnace—typically near 1050°C. The kiln feed is a titanium oxide slurry, created by dissolving either blast furnace slag or ilmenite ore in sulfuric acid and then hydrolyzing the result. This slurry is introduced at the top of the furnace in a continuous feed. The inclination and rotary motion of the kiln cause this material to slowly progress down the inner wall, being gradually “roasted” at increasingly higher temperatures. TiO_2 product falls out of the bottom of the kiln.

The typical transit time for material to pass through the entire kiln is about 12 hours. During this transit, three processes happen sequentially: drying, residual acid removal and calcination. Initially the oxide is in a crystal form known as anatase. In the hottest region of the kiln, much of this is converted into the rutile crystal phase. The end product, consisting of a mixture of these two phases, continuously falls out of the lower end of the kiln. This is subsequently processed to form the ultra-fine pigment powder. The ratio of rutile to anatase is an important measure of product quality for reasons connected to whiteness and durability.

Process control

The goal of process control is to produce a consistent product at maximum throughput. Good control of the kiln is very difficult to achieve due to the inherent complexities of the process. A sophisticated control model has been developed to vary the gas feed rate to the burner.

In the past, slow data sampling rates have limited the ability to use this control package. The reason for this was that previous methods were based on x-ray diffraction, which required

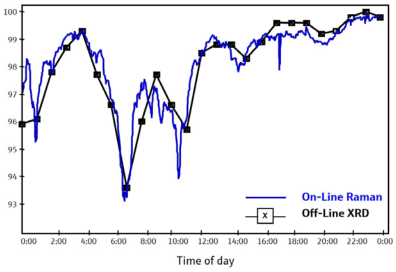

Figure 1: The short data acquisition time of Raman spectroscopy allows real-time process control. Compare the level of detail in data from the on-line Raman spectrometer to that from the off-line x-ray diffractometer (XRD).

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

People for Process Automation

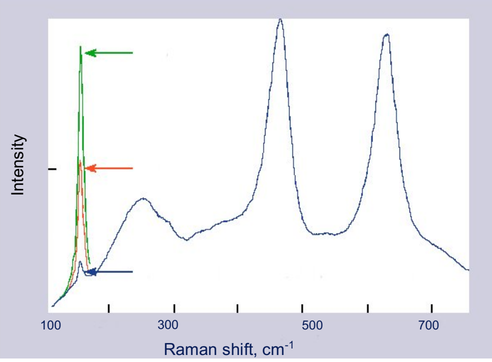

Figure 2: The percent anatase can be directly determined from the area of the characteristic peak at 142 cm^{-1}.

lengthy sample preparation and in any case lacked the precision required. Sampling rates had to be increased by an order of magnitude before good control became possible. The only obvious way of getting this combination of speed and precision was by Raman spectroscopy (Figure 1).

Raman monitoring

The kiln process can now be controlled in real time using a Raman analyzer with a filtered fiber optic probe head.

The small size and extreme hardness of titanium dioxide crystals makes them very pervasive and damaging to even the most hardened instrumentation. Each spectrometer is therefore operated in a sealed enclosure remote from the kiln. Fiber links of 50–100 meters length connect the spectrometer to measurement probes on each kiln.

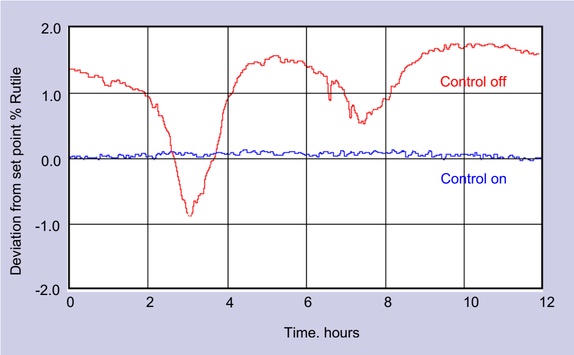

Figure 3: The short response time of Raman sampling enables much tighter process control than was possible using traditional (2 per hour) automated at-line analysis.

Rather than view the process directly with a Raman probe, it was decided to design an automated sampling system. At the kiln output, a screw feed mechanism continuously collects a small amount of product and pushes it across the focus of the Raman probe head. TiO_2 produces strong Raman signals and spectra can be acquired in just seconds. However, because of the small sampling volume (approximately 50 µm diameter) of the probe head, and the fact that the sample is heterogeneous, it is important to make measurements on a statistically representative volume of material. For this reason, for each measurement, spectra are collected and averaged over a three-minute period. The Raman spectra of the two phases are sharp and distinct[1-3] (Figure 2), allowing simple peak areas to be used to derive concentrations (after correction for sample temperature). For each kiln, the rutile/anatase ratio derived from these peak measurements is then fed directly to the kiln controller for true closed-loop operation.

Improvement in control

Figure 3 illustrates the level of control achieved with real-time testing, compared to conventional at-line testing. In addition to maintaining the desired rutile/anatase ratio, real-time control improves the general stability of the process and yields other quality benefits. The biggest gain however has been a marked increase in productivity, because the ability to run a chemical process under steady control allows that process to be run at higher throughput. Also, the resulting improved consistency delivers benefits at all subsequent stages of the process. Although the exact figure is proprietary, the value of this "extra" product is very significant. Raman spectroscopy has proved its value as a process control tool.[1-3]

References

1. King, B.; Clegg, I; Everall, N., *"Increasing TiO2 production by closed-loop Raman,"* Raman Review, Fall 1999.
2. Iida, Y.; Furukawa, M; Aoki, T.; Sakai, T., *"Raman spectrum of ultrafine anatase powders derived from hydrolysis of alkoxide,"* Applied Spectroscopy, Vol. 52, 1998, 673.
3. Lewis, I.R. Process Raman Spectroscopy. In *Handbook of Raman Spectroscopy;* Lewis, I.R., Edwards, H.G.M., Eds. Marcel Dekker: New York, 2001; pp. 41–144

AI01198C/66/EN/01.21