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Investigation and Mitigation of Fumed Alumina Processing Problems

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ABSTRACT

Cabot Corporation produces fumed alumina for a variety of end users. This material consists of elongated, branched, "fractal" particles (aggregates) of ca. 200 nm equivalent spherical diameter, and with high surface areas, 55 to 100 m^2/g, depending on grade. An end user had reported filtration problems with dispersions made from one of the alumina products. This paper describes how polarized light microscopy (PLM) was used to determine that unwanted formation of alpha alumina particles was the main contributor to the filtration problems. A PLM method was then developed to screen the product prior to release.

INTRODUCTION

Fumed alumina is produced using a very high temperature flame hydrolysis process. Anhydrous aluminum chloride feedstock is vaporized, mixed with air, and injected into a natural gas flame at ca. 1700° C. The alumina (Al_2O_3) produced by this process has a "fractal", or aciniform, structure (Figure 1) and consists of aggregrates of ca. 150 nm average equivalent spherical diameter. Each aggregate is composed of several "primary particles", spheres of ca. 15-20 nm diameter, tightly bound to form a branched morphology.

Various grades of fumed alumina, with different surface areas, are produced for a variety of purposes such as paper coatings and fluorescent light coatings. One of the most common grades, the 55 m^2/g product, has been extensively studied to determine its crystalline phase composition. The X-ray diffraction (XRD)

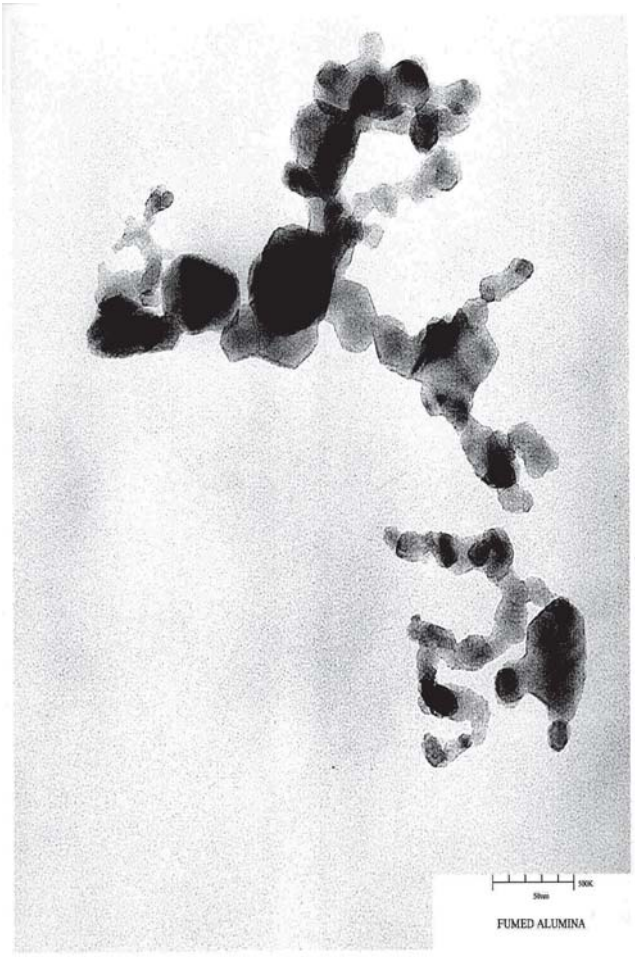

Figure 1: A transmission electron microscope image of a typical Cabot 55 m^2/g fumed alumina aggregate.

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spectrum (Figure 2) is complex due to a mixture of amorphous and 2 major crystalline phases (1):

Theta (q) - 56.5%
Amorphous - 23.9%
Delta * (d*) - 19.6%
Gamma (g) – trace

The amorphous content increases with increasing surface area, e.g. an experimental 200 m^2/g grade was determined to be > 90 % amorphous. The concentration of the alpha (a) phase is normally << 0.1% and is ideally zero, due to properties not desirable for many applications of fumed alumina. Due to the complexity of the XRD spectrum of fumed alumina, however, it is difficult to measure the alpha alumina content by this method, and the method detection limit is, at best, in the order of 0.1%, or 1000 ppm. As described in this paper, this turned out to be insufficiently sensitive to determine alpha alumina at levels that caused processing problems with one of the end-users of our product. We describe how polarized light microscopy (PLM) was used to determine the cause of the problem and the development of a PLM method that we now use for quantitative screening of fumed alumina before release.

PROBLEM DEFINITION, INVESTIGATION AND MITIGATION

Typically, users of the product disperse it into a stable aqueous colloidal suspension (slurry) as the first stage of the process, and usually pass the slurry through a process filter just prior to use. A user had

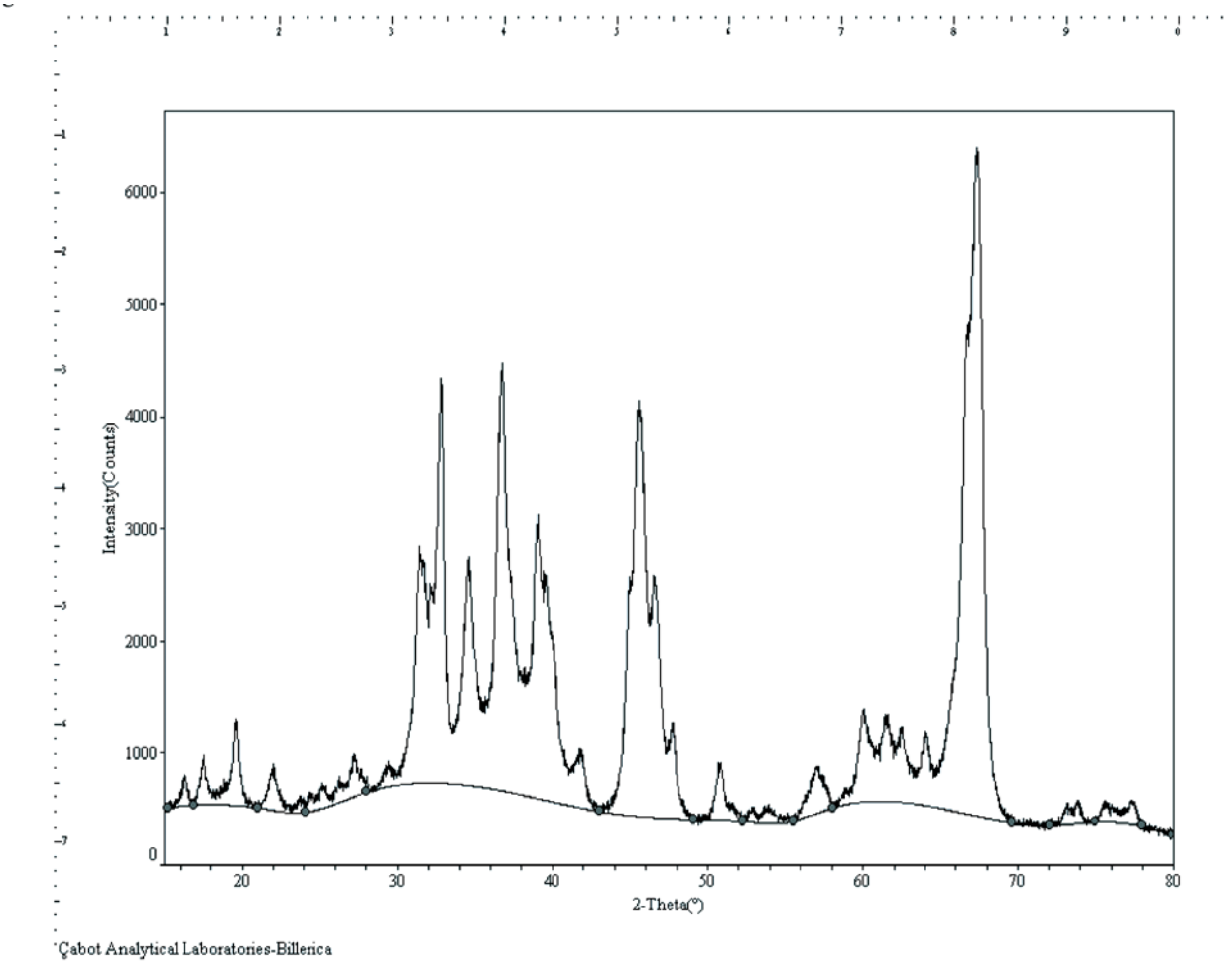

Figure 2: Powder X-ray diffraction (XRD) spectrum of Cabot 55 m^2/g fumed alumina.

reported severe filterability problems for dispersions made from some alumina lots being produced at one of the plants.

Cabot Analytical Labs began the investigation of the problem by microscopical examination of one of the user's process filter residues from the worst performing lot. The large-scale slurry filtration provides a concentration of about 25,000x for particles > 20 μm (nominal filter pore size). We backwashed the filter with deionized water, centrifuged at 300 x g for 30 minutes, re-suspended the resulting residue and re-centrifuged to wash away any adhering fine "normal" alumina particles. We then dried the washed residue using a heat lamp and examined it using PLM.

PLM examination revealed that virtually all the particles in the resulting filter residue concentrate appeared to be alpha alumina (Figure 3). The majority of these had the well-known "vermicular" structure that alpha alumina can exhibit, particularly under high temperature crystallization conditions (2). Other particles showed the hexagonal (or hexagonal segments) structure also exhibited by alpha alumina. We then obtained an XRD spectrum of the filter residue material, which confirmed that it was virtually 100% alpha alumina (Figure 4).

With this information, the plant engineering staff determined that the leading root cause hypothesis was that the alpha alumina arose through problems with the aluminum chloride feedstock. An impurity in the

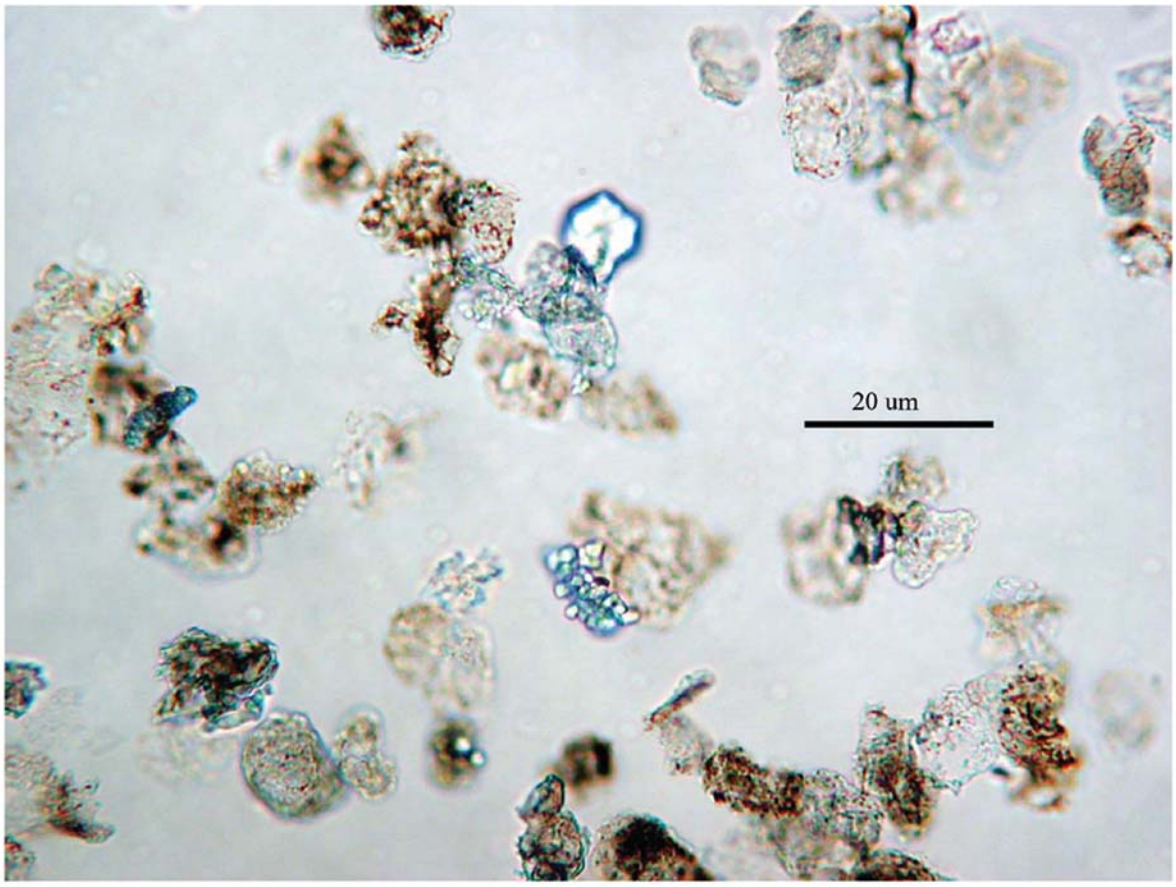

Figure 3: Polarized light microscope image of the residue obtained after backwashing a process filter used for a problem alumina slurry lot. The filter treatment details are given in the text.

feedstock had reacted in the high temperature flame to convert directly to alpha alumina.

In order to test the hypothesis and to evaluate corrective action, we needed to develop a quantitative analytical method to measure the alpha alumina content of fumed alumina at levels below the detection limit of the XRD. A test was developed to concentrate the alpha particles by centrifugation of alumina slurry and obtain a quantitative estimate using PLM refractive index identification + count method. We found that, after the fumed alumina is mixed with water and dried at relatively low temperatures (< 250° C), it appears to convert to hydrated forms that have a refractive index of < 1.70 (3), compared to 1.76 prior to water addition. However, the alpha phase does not undergo this hydration reaction and retains the 1.76 refractive index value. We were therefore able to readily distinguish the alpha alumina particles from the other hydrated alumina forms by PLM examination of a concentrate prepared by centrifuging laboratory-prepared slurry. We prepared the slurry by addition of 10g of fumed alumina to 100 mL of reagent grade water and probe sonicating the mix at the highest power for 7 minutes. After centrifuging for 15 minutes at 300 x g, we poured off the supernatant liquid and re-suspended the centrifuge plug in 3 mL of 100% ethanol using a vortex mixer. We then added 25 µL of the ethanol suspension to a pre-cleaned glass slide, spread the residue as evenly as possible over the slide to match the dimen-

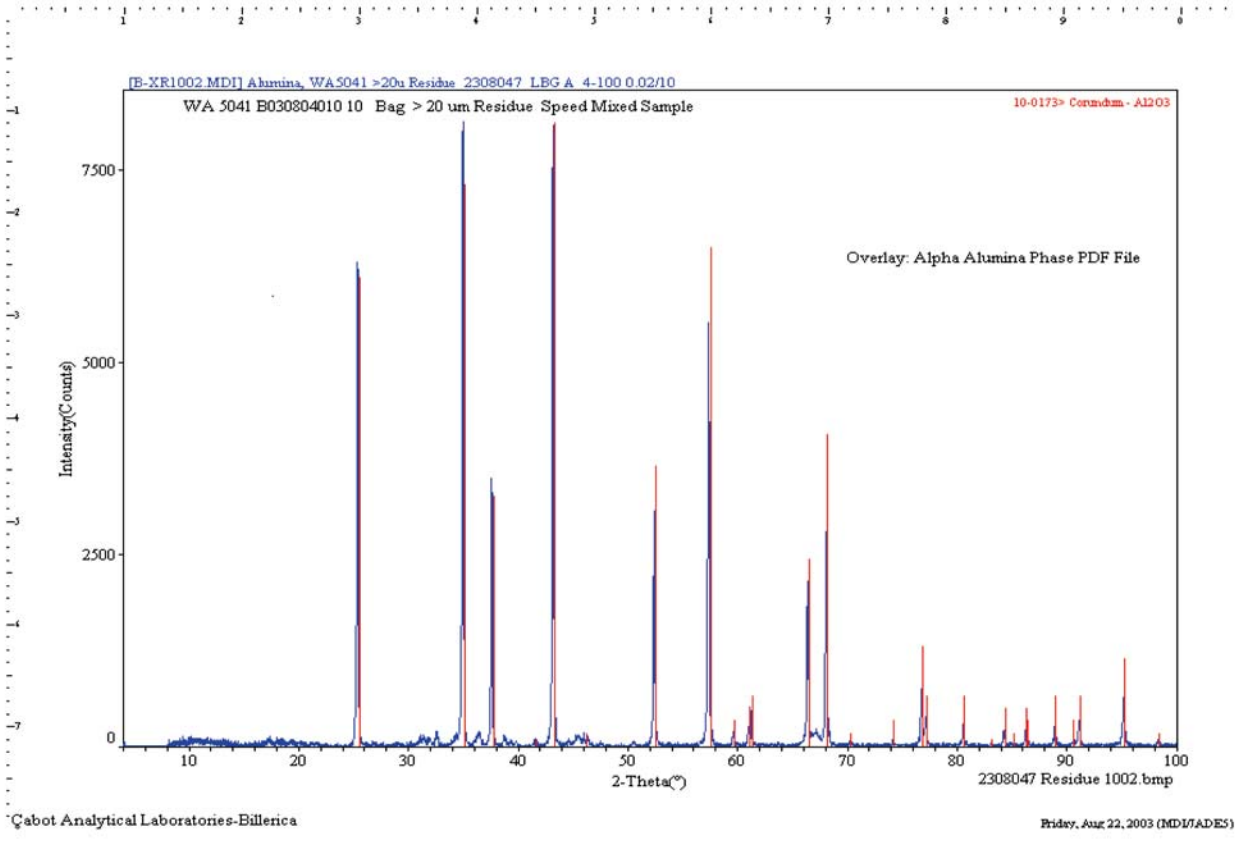

Figure 4: XRD spectrum of the same filter residue as shown in Figure 3. The red trace is the library reference spectrum of alpha alumina.

sions of a cover slip, and added a few μL of Cargille refractive index liquid 1.70, followed by placement of the cover slip. By examining the slide using transmitted polarized light and utilizing the central illumination method (4) for refractive index comparison, we were able to make a very quick identification and count of the alpha alumina particles in the mix.

The test proved to be very successful in predicting the problem that was impacting the supply chain and to assess corrective action. Corrective action was taken in the feed burner control system to prevent the impurity buildup in the feedstock and the problem was immediately remedied (Figure 5).

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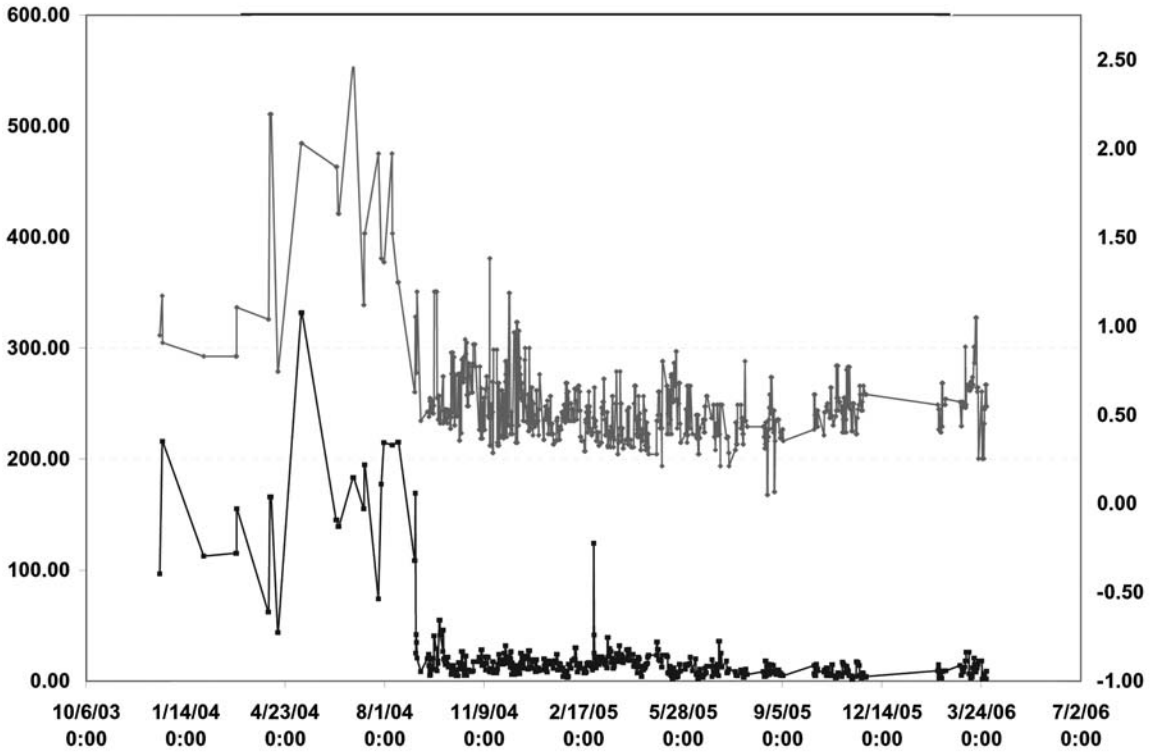

Figure 5: Results from the PLM alpha alumina count test (see text) compared with the end user filter change process data, during the problem period and after the remedial action applied to the fumed alumina production process. Comparison of user process variable (upper plot) and microscopical alpha co-count count (lower plot).