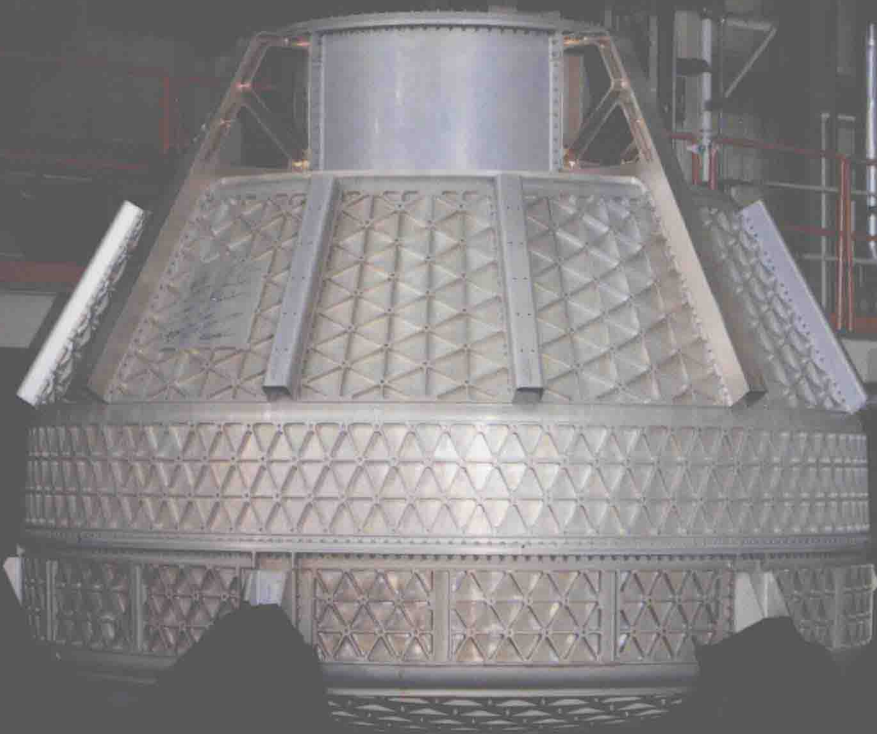


ANALYTICAL TROUBLESHOOTING OF PROCESS MACHINERY AND PRESSURE VESSELS:

INCLUDING REAL-WORLD CASE STUDIES



CHETNA SARASWAT

Analytical Troubleshooting of Process Machinery and Pressure Vessels: Including Real-World Case Studies

Editor

Chetna Saraswat



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Analytical Troubleshooting of Process Machinery and Pressure Vessels: Including Real-World Case Studies

Preface

A highly practical troubleshooting tool for today's complex processing industry, Evolving industrial technology-driven by the need to increase safety while reducing production losses-along with environmental factors and legal concerns has resulted in an increased emphasis on sound troubleshooting techniques and documentation. Analytical Troubleshooting of Process Machinery and Pressure Vessels provides both students and engineering professionals with the tools necessary for understanding and solving equipment problems in today's complex processing environment. It is a practical book that has been used to design and troubleshoot over 90% of the equipment worked. A rough estimate is that the examples in this book have saved over \$50 million in lost production or warranty claims by eliminating repeat failures or by avoiding failures altogether.

Editor

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Chapter 1

Ultra-Rapid Elimination of Biofilms via the Combustion of a Nanoenergetic Coating

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ABSTRACT

Background

Biofilms occur on a wide variety of surfaces including metals, ceramics, glass etc. and often leads to accumulation of large number of various microorganisms on the surfaces. This biofilm growth is highly undesirable in most cases as biofilms can cause degradation of the instruments and its performance along with contamination of the samples being processed in those systems. The current “offline” biofilm removal methods are effective but labor intensive and generates waste streams that are toxic to be directly disposed. We present here a novel process that uses nano-energetic materials to eliminate biofilms in < 1 second. The process involves spray-coating a thin layer of nano-energetic material on top of the biofilm, allowing it to dry, and igniting the dried coating to incinerate the biofilm.

Results

The nanoenergetic material is a mixture of aluminum (Al) nanoparticles dispersed in a THV-220A (fluoropolymer oxidizer) matrix. Upon ignition, the Al nanoparticles react with THV-220A exothermically, producing high temperatures (> 2500 K) for an extremely brief period (~ 100 ms) that destroys the biofilm underneath. However, since the total amount of heat produced is low (~ 0.1 kJ/cm²), the underlying surface remains undamaged. Surfaces with biofilms of *Pseudomonas aeruginosa* initially harboring $\sim 10^7$ CFU of bacteria /cm² displayed final counts of less than 5 CFU/cm² after being subjected to our process. The byproducts of the process consist only of washable carbonaceous residue and gases, making this process potentially inexpensive due to low toxic-waste disposal costs.

Conclusions

This novel method of biofilm removal is currently in the early stage of development. However, it has potential to be used in offline biofilm elimination as a rapid, easy and environmentally friendly method.

BACKGROUND

A biofilm is defined as a microbially derived sessile community characterized by cells that are irreversibly attached to a substratum or interface or to each other; are embedded in a matrix of extracellular polymeric substances that they have produced; and exhibit an altered phenotype with respect to growth rate and gene transcription [1]. Biofilms can occur spontaneously (without deliberate intention to grow them) on a wide variety of surfaces such as metals, plastics, glass, ceramics, wood and cement. Once established, they can accommodate a large number of bacteria per unit area of the surface. While $\sim 10^5 - 10^7$ CFU (Colony Forming Units) of bacteria /cm² are commonly encountered, numbers as high as $10^9 - 10^{10}$ CFU/cm² have been reported [2,3].

Their presence may be undesirable in a variety of applications. For instance, on ship hulls, the formation of a microbial biofilm can raise the drag coefficient by as much as 29% [4], contributing to correspondingly higher fuel usage. In heat exchangers and cooling water systems, which are an integral part of a wide variety of industrial processes, a 250 micron thick layer of biofilm may reduce the effective heat transfer coefficient of a heat exchanger by as much as 50% [5]. In addition, the metabolism of bacteria in the biofilm (production of carbonic, pyruvic, citric, lactic and other acids) causes a reduction in pH at the surfaces, leading to enhanced rate of chemical corrosion [6]. This inflicts additional economic burdens such as the need for premature replacement of equipment and unscheduled downtime to clean fouled equipment [7]. In the oil and natural gas industry, bacterial biofilms cause financial losses of \sim \$100 Million each year through the corrosion of pipelines and process equipment and souring of reservoirs [8]. In the paper manufacturing industry, biofilms are responsible for an estimated 10-20% of all machine downtime[9]. Thus, there are huge incentives to (a) prevent biofilm formation, and (b) to minimize their growth rate during operation of a wide variety of process equipments like tanks, transport tubing, and heat exchangers. Consequently, several approaches have been explored in the past. These approaches include the use of materials and coatings that hinder biofilm formation and growth, the continuous or pulsed addition of chemicals such as acids, oxidizers or enzymes to the process fluid, and the intermittent use of mechanical cleaning agents like scrubbing balls. Despite these efforts,

it is almost impossible to completely prevent biofilms from getting established, and as a result, adversely affecting the performance of the equipment [10]. Once the performance of the equipment falls below acceptable levels, they have been taken offline for biofilm removal.

The offline removal of biofilms from process equipment is also a difficult task. The common methods adopted for the offline removal of biofilm from process equipment [10] can be broadly classified into mechanical and chemical processes. The most common mechanical processes include water/steam/sand blasting for large exposed surfaces (blasting being the process of forcibly propelling a stream of material against a surface under high pressure) and abrasive pads for smaller, more difficult to reach surfaces such as the interior of tubes. The main disadvantages of using mechanical processes are that they are labor intensive and take a long time. The latter is especially undesirable, as in many cases, the whole process remains shut for the duration during which one or more of the equipments are brought offline, resulting in losses of tens of thousands of dollars an hour. The other alternative is to use strong chemical cleaning agents like acids, alkalis, and strong biocides. Strong chemicals are often required because the biofilm's extracellular matrix prevents milder chemicals such as antibiotics and germicides from acting on the cells embedded within it. The use of chemicals for biofilm removal has its own advantages and disadvantages. While they are usually less labor intensive, relatively faster, and can act on hard-to-reach surfaces, they are often expensive. Moreover, the use of strong chemicals can also result in the generation of waste-streams that are expensive to dispose off due to their toxicity.

Thus, there is a need for an offline biofilm-removal process for process equipment that is fast, effective, economical, and yet environmentally friendly. Table 1 lists numerous approaches (ultrasonication, electric fields, mild chemicals such as enzymes, and their combinations [11-17]) that have been employed and reported by other groups for this purpose. As can be seen, their efficacy is limited (they achieve only 1 to 3 \log_{10} reductions in the number of viable bacteria per unit area) and/or take a long time (hours). In contrast, if our proposed method were employed for the same application (offline removal of biofilms from process equipment), the biofilm removal could be potentially completed faster (in minutes), and with greater efficacy ($> 5 \log_{10}$ reduction in the number of viable bacteria).

Table 1: Efficacy of various environmentally friendly processes used for the removal of biofilms

| Biofilm type | Method used for biofilm elimination | Log reduction in CFU count | Time taken |
|---|--|--------------------------------|---|
| <i>P. aeruginosa</i> and <i>S. aureus</i> | Cleaning with detergents, followed by high-pressure wash and mechanical scrubbing [11] | < 3 | 20 min soak detergent + 1 min wash + <1 min scrub |
| <i>P. aeruginosa</i> and <i>K. pneumoniae</i> | Treatment with multiple chemicals (chelating agents, hypochlorites etc.) [12] | 1–3 depending on chemical used | 1 hr |
| <i>Pseudomonas fluorescens</i> | Combination of Enzymes (proteolytic + polysaccharide-degrading enzymes) [13] | 2-4 | 2 hrs |
| <i>P. aeruginosa</i> , <i>S. epidermidis</i> , and <i>S. aureus</i> | Ultrasound [15] | 1.02 – 1.48 | 10 minutes |
| <i>E. coli</i> and <i>S. aureus</i> | Chelating Agents (EDTA / EGTA) and Ultrasound [14] | ~ 2 | Unknown soak time; 10–60s sonication |
| <i>Pseudomonas aeruginosa</i> | Biocides (Chemicals) + Electric Field [16] | 3 | 12 hours |
| <i>E. coli</i> | High Pressure CO ₂ / N ₂ aerosols [17] | 1-2 | 90 s |
| <i>P. aeruginosa</i> | Our Method (Rapid combustion of a sprayed on layer of nano-energetic materials) | > 5 | ~ 1 min spray; < 1 s burn |

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We present here a novel material and method that is able to outperform the methods listed in Table 1 in both speed and efficacy. Briefly, we use an optimized blend of Al nanoparticles (fuel) in a fluoropolymer (oxidizer) matrix that is spray-coated onto the surfaces, and which burns away extremely rapidly ($< 1 \text{ sec/cm}^2$), generating very high temperatures [2200–3200 K [18]] that destroys the biofilm, but leaves the underlying surface intact. The underlying surface remains unaffected because the amount of heat released is not very high: $\sim 0.1 \text{ kJ/cm}^2$, according to our estimates based on the heat of combustion of Al [19], and the known loads of Al nanoparticles in our formulation. The key to the efficacy of the process lies in the use of Al nanoparticles with average size of 80 nm and narrow size distribution. The nanometer

size of Al particles not only enables the rapid release of the heat of combustion (significantly reduced mass transfer limitation) along with the generation of high temperatures, but also allows us to spread a small mass of Al (~ 10 mg) uniformly over the test areas (~20 cm²). The latter limits the amount of heat released, which, in turn, limits the damage done to the underlying substrate. We demonstrate the efficacy of this technique using *Pseudomonas aeruginosa* biofilms grown at moderate shear as our model biofilm. *P. aeruginosa* was chosen because it has been extensively studied [20], and to compare our technique to those of other researchers [11-13] who report the efficacy of their biofilm removal/killing methods using *P. aeruginosa* biofilms.

METHODS

Cultivation of Model Biofilms on Substrates of Interest

We cultivated *P. aeruginosa* biofilms on a variety of substrates such as metals (steel and brass), ceramics (bathroom tiles), and glass that can be expected to withstand the high temperature generated during the burning process for a very short duration.

Above-mentioned substrates with dimensions of 1" × 3" served as our test coupons (except for the ceramic, for which a 2" × 2" piece was used instead). These substrates were first thoroughly cleaned to ensure no pre-existing biofilm. A 1% (w/v) solution of detergent was prepared, and the substrates were first cleaned by sonicating them in this solution for 10 minutes using an ultrasonic bath. The detergent solution was then replaced with DI water and the substrates were sonicated for an additional 10 minutes. The substrates were then rinsed with DI water and then placed in 2 M HCl (for glass and ceramic), or bleach solution (for metals). The substrates were then sonicated again in DI water and rinsed. Finally, they were air-dried in a Biological Safety Cabinet.

Cultures of *P. aeruginosa* were obtained from commercial sources (Ward's Natural Sciences), and an aliquot was inoculated into 10 ml of TSB (Tryptic Soy Broth) and incubated overnight with shaking at 37°C. The resulting log-culture had a concentration of ~10⁹ CFU/ml. The bacterial cells were isolated by centrifugation, and re-suspended

in an equal volume (10 ml) of 1× Phosphate Buffered Saline (PBS) (a buffer consisting of Sodium Chloride and Sodium Phosphate). This suspension of bacteria was then introduced into a sterile (autoclaved) vessel with a capacity of ~1 L loaded with ~500 ml of 1/10× TSB. Multiple (four to six) coupons of a particular material (metal, glass or ceramic) were prepared by covering one side with a piece of adhesive backed silicone rubber sheet, loaded into the tank with the exposed side upwards (in contact with the liquid), the top of the tank covered in saran wrap, and the tank placed in an incubator-shaker. The incubator shaker was operated at room temperature (~ 25°C) with an oscillation speed of 200 rpm, which corresponds to a shear rate of $\sim 10^5 \text{ s}^{-1}$ at the fluid-solid interface (biofilm). The biofilm was allowed to form over a period of 4 days. At the end of this period, during which there was perceptible growth of biofilm in the system, the coupons were extracted, washed in DI water to remove cells that adhere weakly to the surface (those not within the biofilm matrix) and loaded into individual Ziploc™ bags (pre-sterilized by wiping with 70% ethanol and exposed to UV radiation in a biological safety cabinet) and stored in refrigerator (4°C). They were then used (within a period of 3 days) for further testing. It may be noted that the biofilms still retain their characteristic slimy appearance after retrieval from storage, indicating that they remain in a hydrated state.

The Biofilm Removal Process

Our proposed process to eliminate biofilms from substrates of interest is illustrated schematically in Figure 1. As shown in Figure 1, we begin the process by dissolving a known amount of THV 220A in acetone using sonication. THV 220A is a commercially available (3 M, St. Paul, MN) fluoropolymer, composed of tetrafluoroethylene, hexafluoropropylene and vinylidene-fluoride. Al nanoparticles are then added to this solution and dispersed homogeneously using an ultrasonic bath. The fluoropolymer plays the role of oxidizer and the Al nanoparticles plays the role of fuel in the nanoenergetic composition. The amount of acetone used in the dispersions was varied as 7, 8, and 10 ml for a total mass of 500 mg of THV 220A polymer and Al nanoparticles. The amount of Al nanoparticles and THV 220A were varied suitably so that the weight ratio of Al to THV 220A was kept at 1:9, 2:8, and 3:7. The nanoenergetic dispersion was then sprayed

uniformly on top of the surfaces of interest (biofilm-covered surfaces of different materials). The acetone evaporates rapidly, leaving behind a dry, paint-like coating on the surface. In order to keep the thickness of the coating nearly the same on any given substrate, the same volume (7 ml) of fluoropolymer/nanoparticle and acetone blend was uniformly used, yielding nanoenergetic coatings 80–100 microns thick. The dried layer was then ignited at one corner using a small flame-torch. The flame self-propagated extremely rapidly, and consumed the whole coated surface ($\sim 3 \text{ inch} \times 1 \text{ inch}$), after which it exhausted itself. The whole process (initiation, propagation, and quenching /exhaustion) took less than 1 second for the surfaces tested ($1 \text{ inch} \times 3 \text{ inch}$ pieces), and left behind a dark, flaky residue, which could be blown away and/or rinsed off to obtain the clean, biofilm-free surface underneath. Based on our earlier studies of the similar blends for other applications [21], the residue is believed to be carbonaceous, with minor amounts of aluminum oxide. (Most of the aluminum is oxidized to AlF_3 by the fluoropolymer). The amount of acetone and the weight ratio of Al nanoparticles to THV 220A were optimized by observing how well the flame self-propagated upon ignition throughout the surface. More importantly, during this optimization, it was ensured that the swiftly propagated flame only destroyed the biofilm, while not significantly damaging the substrate underneath.

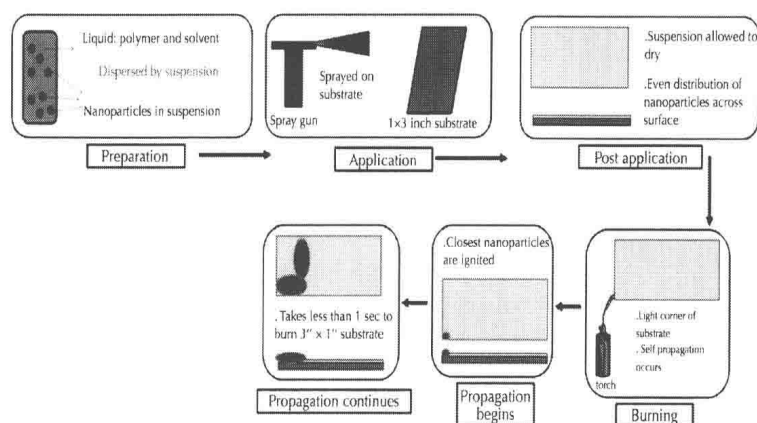


Figure 1: Represents the schematic of the proposed process for ultra-rapid removal of biofilms, which involves spray coating the nanoparticles in suspension onto the substrate containing biofilm, followed by burning the entire surface of the substrate by initiating the ignition of one of its corners.