The Use of Peracetic Acid
At Increased pH Levels

Peracetic acid (PAA) is a weak organic acid but is a strong oxidizing chemical that has unique biocidal properties. PAA is susceptible to hydrolysis, known as *dissociation*. Most weak acids such as PAA are preferentially used below the mid-point of their dissociation constant, known as the pK_a, which is expressed in pH units. PAA is commonly used below the pK_a (pH 8.2-8.4) to minimize the loss of effectiveness and/or the efficiency of the acid.

Commercially available formulations of PAA are equilibrium solutions of acetic acid, peracetic acid and a small amount of hydrogen peroxide. These equilibrium PAA formulations are diluted and used in poultry chillers. The diluted PAA in poultry chillers has an unadjusted or "natural" pH of about 4.5-6. In the long term, hard water has no effect on the pH due to the acidity provided by the equilibrium PAA. Like most acids, PAA is usually used at its unadjusted pH. However, Enviro Tech has found that PAA solutions are unexpectedly effective at higher pH ranges and provide significant benefits not seen at "typical" pH ranges found in poultry chiller systems.

The poultry chilling process is by far the largest point-of-use for PAA and is arguably the most important HACCP operation in the poultry facility and is the focus of this discussion. The following is an overview of the benefits and advantages of using PAA at increased pH levels.

Health and Safety:

In recent years, the vapor odor of PAA solutions used in poultry processing plants has come under scrutiny as a potential problem for both workers and inspectors in the industrial environment. As referenced above, equilibrium PAA formulations provided by commercial suppliers contain both acetic acid (vinegar) and peracetic acid, both of which are volatile and can escape into the atmosphere. These compounds can be irritating in the vapor phase because both compounds are very closely related in structure, and the acetic acid moiety is quite volatile at or near its pK_a *acid dissociation constant*, which is pH 4.7. However, at an increased pH level of about 6.0 the acetic acid portion of the PAA formula (which can be 3x more concentrated than the PAA concentration) becomes completely dissociated and ionic in nature and is not volatile. The pK_a of peracetic acid is pH 8.2-8.4 depending on the temperature of the solution (ambient pKa is 8.2, cold PAA is 8.4). Therefore, at pH 8.4 in poultry chillers, 50% of the peracetic acid is dissociated (ionized). The other 50% is undissociated (active) PAA.

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In summary, considering the pK_a *dissociation constant* of acetic acid is pH 4.7 and peracetic acid is pH 8.4, a functional solution of chiller water at a pH of 8.4 would be about 60-65% less volatile than the same PAA solution at pH 5, (which is the natural pH of an unadjusted PAA solution in poultry chillers). At pH levels above the pK_a an acid becomes ionic (dissociated) and cannot volatilize into the gas phase. This can also be termed as the vapor or volatility potential. The volatility potential is directly proportional to the potential odor so this reduction in odor at higher pH levels is a major health and safety improvement vs. pH unadjusted PAA solutions.

Efficacy:

Microbial reduction of *Salmonella spp*. on poultry is a key concern for the industry, so it was decided to perform testing on *Salmonella* under conditions similar to those found in poultry chiller systems, which primarily are low doses and long contact times. This type of testing would determine the *relative* efficacy of PAA over time at various pH levels as well as establish if Salmonella spp. are less or more difficult to kill at higher pH levels.

A series of experiments were designed by the authors that challenged *Salmonella* with a 5 ppm nominal dose of PAA in a solution containing 0.5% organic load (chicken serum) at several pH levels. The exposure times were 0, 1, 5, 10, and 20 minutes. The pH ranges chosen were 5, 7, 8, 9 and 10. The following are the results for one set of data that is representative of the data series.

5 ppm nominal PAA

$\log_{10}$ remaining (*Salmonella typhimurium*, CFU/ml)

	0 min	1 min	5 min	10 min	20 min
pH 5	7.34	6.51	2.09	1.59	1.23
pH 7	6.95	5.59	2.21	1.56	1.74
pH 8	6.95	6.77	0	0	0
pH 9	6.95	6.74	5.85	0	0
pH 10	6.95	7.0	7.1	6.85	6.65

It can be seen clearly that the experimental dose of 5 ppm PAA at pH 8 and pH 9 outperform the low and high bracket pH ranges of pH 5 and pH 10. This data is represented as Table XXII, Page 21, in a patent application published on Sept. 27, 2012 (US2012/024461 A1).

At a pH of 8, about 55-60% of the initial PAA dose would be available (undissociated) for disinfection, yet the challenge data suggest that pH 8 is clearly superior vs. pH 5 and pH 7 even at roughly half the undissociated PAA concentration. This indicates a very strong correlation between the pH of the PAA solution and the increased sensitivity of *Salmonella* at elevated pH levels to biocidal kill. Peracetic acid clearly shows superior biocidal performance at pH ranges between 8 and 10 compared to pH < 7 under similar conditions found in poultry chillers.

The data also shows that PAA at unadjusted pH levels begins to work earlier than the more alkaline pH ranges: for example: see pH 5 and pH 9 data at five minutes contact time (2.09 $\log_{10}$ CFU/mL remaining vs. 5.85 $\log_{10}$ CFU/mL remaining, respectively). However, what the data also suggests is that the PAA may be consumed faster at lower pH levels which would make it unavailable for disinfection for the longer contact times (e.g.at 10-20 minute contact). This indicates that longer exposure times to pH-adjusted PAA containing water in chiller systems are advantageous, which makes the application in poultry chiller systems a prime candidate for pH adjustment.

In another experiment, *Campylobacter jejuni* was challenged against 10 ppm nominal PAA. The results are reported below and on Table XXXIV (Page 26) of the patent application mentioned above. No particular sensitivity or desensitivity to lower concentrations of PAA (such as in chillers) at any pH level considered was observed. However, the efficacy differences at the various pH levels between pH 6-8 were statistically insignificant, which resulted in similar efficacy regardless of the pH.

10 ppm nominal PAA

Log10 remaining (Campylobacter jejuni CFU/ml)

	0 min	20 min
pH 6	6.98	3.93
pH 7	6.98	3.72
pH 8	6.98	4.0
pH 9	6.98	4.96

Campylobacter, unlike Salmonella, is not pH sensitive. It is *concentration* dependent. It appears that Campylobacter is more resistant to eradication by PAA at any pH. However, the reduction in efficacy at pH 9 can be adjusted for easily during processing by increasing the undissociated PAA dose in accordance with the pK_a as explained above. It should be noted that although there is significant increase in sensitivity by Salmonella spp. at increasing pH levels, that *Campylobacter* efficacy is not compromised in the process, and remains constant through most of the pH ranges under consideration.

Organoleptic Observations:

In the past few years since alkaline PAA solutions have been used there is clearly a visual improvement to the quality of birds that exit the chiller systems compared to chlorine or unadjusted PAA applications. There have been improvements in color, texture, tenderness and general appearance. All facets of organoleptic consumer quality have been improved.

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