CHAPTER 4

Temperature Effects on Iron Corrosion

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KEY WORDS: iron corrosion, temperature

ABSTRACT

Temperature is an often overlooked water quality parameter that may influence corrosion of iron pipes in drinking water distribution systems. This study examined corrosion of cast iron samples in an aerobic, microbially stable water at different constant temperatures (5, 20, and 25°C) as well as in waters where the temperature continuously cycled (17.5 – 23°C and 5 – 20°C). The composition and morphology of scale formed at the three different constant temperatures showed large differences, and the 5°C experiment had more weight loss, higher iron concentrations in the water, and more tuberculation compared to 20 or 25°C. However, little difference was observed in the temperature cycling experiments.

INTRODUCTION

Many parameters that influence corrosion can vary with temperature: dissolved oxygen (DO) solubility, solution properties (e.g. viscosity and ion mobility), ferrous iron oxidation rate, thermodynamic properties of iron scale (leading to formation of different phases or compounds), and biological activity.[1] Moreover, heterogeneous iron scale formed on pipes may have large differences in physical properties such as scale density (as described by the Pilling-Bedworth ratio, PBR) and coefficients of thermal expansion.[2] If the scale is exposed to temperature gradients or cycling, these differences might cause mechanical stresses in the scale, leading to spalling or sloughing of scale into the water as corrosion by-products.

Only a few studies have examined the role of different temperatures in distribution system iron corrosion. In general, studies of distribution systems found the manifestations of corrosion to be less severe in colder winter months; for example, lower iron concentrations and corrosion rates[3] and fewer customer complaints of red water[4, 5] were observed in winter. Also, one laboratory study found decreased weight loss for iron samples held at 13ºC versus 20ºC.[6]

Finally, two pilot scale studies observed peaks in turbidity[7] and metal concentrations[8] that appeared to correlate with temperature changes when pipes were exposed to a temperature cycle.

The goal of this study was to examine the effect of both different constant temperatures and temperature cycling on iron corrosion in carefully controlled laboratory experiments.

MATERIALS AND METHODS

Cylindrical pieces of cast iron bar, each 1" in diameter and ¾" long (Grammer, Dempsey & Hudson, Inc, Newark, NJ) were coated with epoxy (Epofix Resin, Struers, Westlake OH), leaving only the top flat surface exposed. Twenty-eight samples were placed in a closed 12-L polycarbonate container completely filled with water. The resulting iron surface area to water volume ratio is relatively low, equivalent to that of a 5-m diameter pipe. Five of these containers were placed in a 5°C constant-temperature room and held at different constant temperature (5, 20, or 25°C) or cycled continuously (17.5 – 23°C and 5 – 20°C). The higher temperatures were maintained with thermostatically controlled aquarium heaters.

The synthetic water was made from distilled water, with 215 mg/L as $CaCO_3$ alkalinity, 100 mg/L Cl^-, and 100 mg/L SO_4^{-2} added from reagent grade sodium salts. The containers were constantly stirred at 250 rpm and covered with black plastic to exclude light (to minimize algal activity and photo-oxidation). A Horiba U-22 Water Quality Monitoring System (Horiba Instruments Incorporated, Irvine, CA) continuously logged water quality data to a computer, including pH, conductivity, turbidity, dissolved oxygen, temperature, total dissolved solids (TDS), and oxidation-reduction potential (ORP). Each day, the pOH was adjusted to 6 ($pH \approx 8$) by addition of saturated CO_2 solution or stripped air and a water sample was collected. Water samples were analyzed for ferrous iron on a Hach DR2010 spectrophotometer (Hach, Loveland, CO), as well as for total iron and total phosphorus using ICP-ES (JY Ultima, Jobin-Yvon, Edison NJ). The water in each experiment was replaced every 14 days with fresh solution.

After 133 days (4.5 months), the samples were removed from the water and dried in a dessicator for one week. The scale (rust) was removed from the surface of each sample,[9] and the sample was weighed to determine total weight loss. The scale was analyzed using X-ray diffraction (XRD, Scintag Series 2000, Scintag, Sunnyvale, CA), and electron microprobe (Cameca SX-50, Cameca Inc., France), and then digested in a 5% nitric acid solution.

RESULTS

The results are divided into two sections: the experiments at three different constant temperature (5, 20, and 25°C) and the experiments where the temperature was cycled (17.5 – 23°C and 5 – 20°C).

Different Constant Temperatures

This particular water quality was chosen because of its expected corrosivity, and within 12 hours a thick orange-brown scale layer had formed on all of the fresh iron surfaces. Only two water quality parameters showed significant differences between the three experiments—pOH and ORP (oxidation-reduction potential). The pOH in the 20°C and 25°C experiments tended to decrease approximately 0.1 pH units each day, which is consistent with the production of OH^- from the reduction of dissolved oxygen:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4\text{-}1)$$

In contrast, the pOH in the 5°C experiment remained nearly constant. This could be the result of the formation of a hydroxide-bearing solid (such as $Fe(OH)_2$ or $Fe(OH)_3$), which consumes the OH^- that is produced. Alternatively, carbon dioxide solubility is higher at 5°C, which may increased dissolved CO_2 and buffer pH changes.

Significant differences were also observed in ORP, which is an indicator of the redox conditions in the system (higher ORP indicates more oxidizing conditions). The ORP in the warmer experiments stayed nearly constant at 215 mV at 20°C and 250 mV at 25°C. In contrast, the ORP in the 5°C experiment consistently dropped sharply down to 50 – 90 mV. This lower ORP is surprising, because dissolved oxygen concentrations are higher at lower temperature, which would tend to keep the ORP high. While these lower ORP values may be indicative of more reducing conditions, no ferrous iron (< 0.01 mg/L) was present in any of the experiments.

Iron Release. One consistent trend was that the 5°C experiment released more iron to the water (Figure 4-1). By the end of the two-week period shown, the iron concentration in the

5°C experiment was six times higher than the 20°C experiment and ten times higher than the 25°C experiment. This trend of higher iron concentrations at lower temperature was maintained throughout most of the experiment. The iron concentrations were relatively low (< 1 mg/L) in this experiment due to the low surface area to volume ratio. However, if similar iron release was assumed for a 0.5-m pipe (a typical water main), the concentrations would be roughly 20 mg/L, which is high enough to cause significant red water problems.

Iron Scale. After the experiments had been running for 133 days (4.5 months), the iron samples were removed from the water. Significant differences were observed in the morphology of the scale formed at different temperatures (Figure 4-2). Iron samples at 5°C had the thickest scale (average of 3 to 4 mm thick) with many bulbous tubercles. Scales formed on iron samples at 20°C and 25°C were similar to each other, with a more uniform texture and a thickness of only 0.5 to 1 mm.

Three typical scale samples formed at each temperature were digested in a boiling 5% nitric acid solution and then measured for total iron and silica using ICP-ES. When the scales were digested, they formed solutions of varying colors; the 5°C samples were green, the 20°C samples were yellow, and the 25°C samples were orange (Figure 4-3). Interestingly, all of the color was removed when the samples were filtered through a 0.45-μm filter; the filtrates were clear. The colored portion of the scale retained on the filters after digestion was between 2 and 8% of the total scale mass. Moreover, when the samples were analyzed for total iron and silica, the filtrate from each of the three temperatures had approximately the same composition.

Thus, it appeared that the color differences at each temperature were due to a relatively small insoluble fraction of the scale—the portion removed by the filter. The bulk scale samples and the solids retained on the filters were analyzed by X-ray diffraction and electron microprobe. Unfortunately, the scale samples were largely amorphous, so x-ray identification of crystalline phases was not possible. In addition, quantitative electron microprobe analysis was not successful due to difficulties in sample preparation. However, given the large differences in color, it seems clear that these recalcitrant solids had different compositions.

Weight Loss and Scale Build-Up. The amount of scale built up on each sample was calculated by comparing the weight of the sample after drying to the weight of the sample after the scale had been removed. The overall weight loss for each sample was calculated by weighing the sample after all the scale had been removed and comparing to the initial weight before the sample was exposed to water. The amount of scale built-up on the 5°C samples was slightly higher (9%) than at 20 or 25°C (Figure 4-4). This scale at 5°C had to be less dense, because the iron content was the same as the warmer temperatures (Table 4-1), yet the volume was clearly much greater (Figure 4-2). The average overall weight loss at 5°C was 16% higher than at 20°C and 23% greater than at 25°C. The differences were significant at 95% confidence based on 24 to 26 replicate samples at each temperature, and amounted to 0.5 – 0.6 % of the original mass of the iron samples.

It is interesting to note that while the differences between colder and warmer experiments were statistically significant, they were not very large (i.e. not order-of-magnitude in scale). Moreover, the trend of worse corrosion at cold temperature is opposite of previous studies, which found more iron corrosion problems at warmer temperature. There are several potential causes for discrepancy, including differences in biological activity.[10, 11] Another possibility is the effect of silica. These experiments had very low (< 1 mg/L) silica in the water, whereas most real systems have higher natural silica levels. Preliminary experiments indicate that not only does silica dramatically increase iron corrosion, but at higher silica levels the effect of temperature is switched (more corrosion at higher temperature). Finally, these experiments were relatively short-term; the relative effect of different temperatures may change as the samples continue to age.

Temperature Cycling

Two other experiments were set up as above, except that the temperature was cycled continuously (17.5 – 23°C and 5 – 20°C) by turning the heater on and off at set intervals. During the initial phases of this experiment, turbidity (a surrogate for iron concentration) was monitored every hour with the water quality multi-probe. The hope was to replicate the results observed by Smith[7] where peaks in turbidity correlated with inflections of the temperature cycle. Indeed, the same phenomenon was observed here; as the temperature was cycled between 17.5 and 23°C the turbidity cycled ± 3 NTU, directly out of phase with the temperature cycle (Figure 4-5). Similar results were obtained for the 5 – 20°C cycling experiment, with the turbidity cycling ± 10 NTU.

However, when turbidity was measured with a standard laboratory bench-top turbidimeter (Hach 2100N, Hach, Loveland CO) instead of the multi-probe, this cycling of turbidity was not observed. Moreover, when water samples were collected every hour, no cycling was observed in measured iron concentrations. It was ultimately determined that the observed variations in turbidity with the multi-probe were actually a measurement artifact: temperature affects the detector the multi-probe uses to measure turbidity. Thus, dramatic changes in turbidity or iron concentration did not occur with temperature cycling in this study, although this phenomenon could be occurring in other systems.

The two temperature cycling experiments also did not show dramatic differences in iron release or weight loss. In fact, the results for each cycling experiment fell between the results for each constant temperature endpoint. For example, the iron concentrations in the 5-20°C experiment were typically less than iron levels in the 5°C constant temperature experiment, but greater than the 20°C experiment. Similar results were obtained for weight loss. The weight loss at 5°C was greater (at 95% confidence) than at 20°C, but the weight loss in the 5-20°C cycling experiment was not statistically different from either 5°C or 20°C (Figure 4-6). There was no statistical difference in weight loss for the warmer constant temperatures and cycle.

Thus, catastrophic spalling of scale with changing temperature did not occur in these tests, although the general hypotheses remain valid and might be important in other waters. In addition, the curved surface of a pipe will likely be more susceptible to physical phenomena associated with temperature cycling than the flat coupons used in this study.

SUMMARY

Clear differences were observed in the corrosion of iron at different temperatures. In this study, samples held at 5°C had higher iron concentration, more tuberculation, and increased weight loss compared to samples at 20°C or 25°C. This is due to variations in the composition and morphology of scale formed at each temperature. Temperature cycling did not significantly impact iron corrosion compared to different constant temperatures. Overall, the observed differences in corrosion with temperature were relatively small, although larger differences may be found in other systems.

ACKNOWLEDGEMENTS

The authors are grateful to Siyuan Chen and Jason Rushing for laboratory assistance in this study. This work was supported by the National Science Foundation (NSF) under grant BES 9796299. The opinions, findings, and conclusions or recommendations are those of the authors and do not necessarily reflect the views of the NSF. The first author was supported by the American Water Works Association Wolman Fellowship and the Virginia Tech Via Foundation.

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Table 4-1: Mass composition of the soluble portion of the digested scale.

Samples	Iron (%)	Silicon (%)
5°C	57.4 ± 0.3	1.22 ± 0.04
20°C	57.7 ± 0.7	1.13 ± 0.04
25°C	56.6 ± 1.6	1.04 ± 0.03

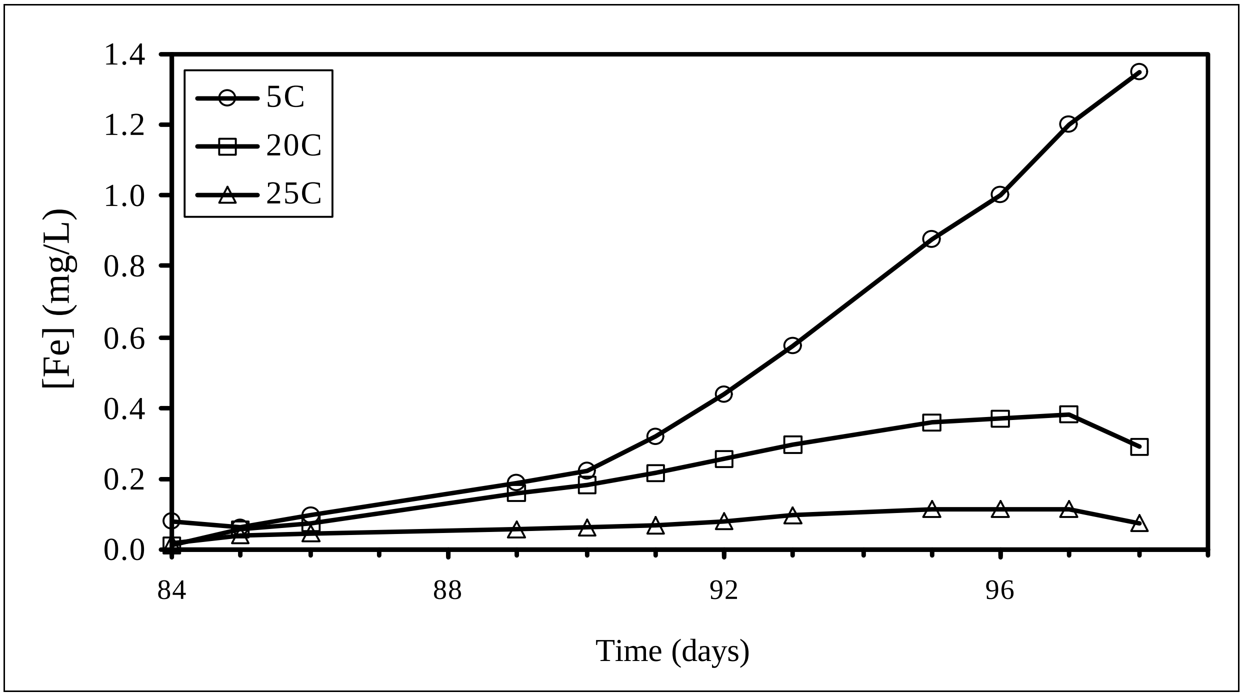
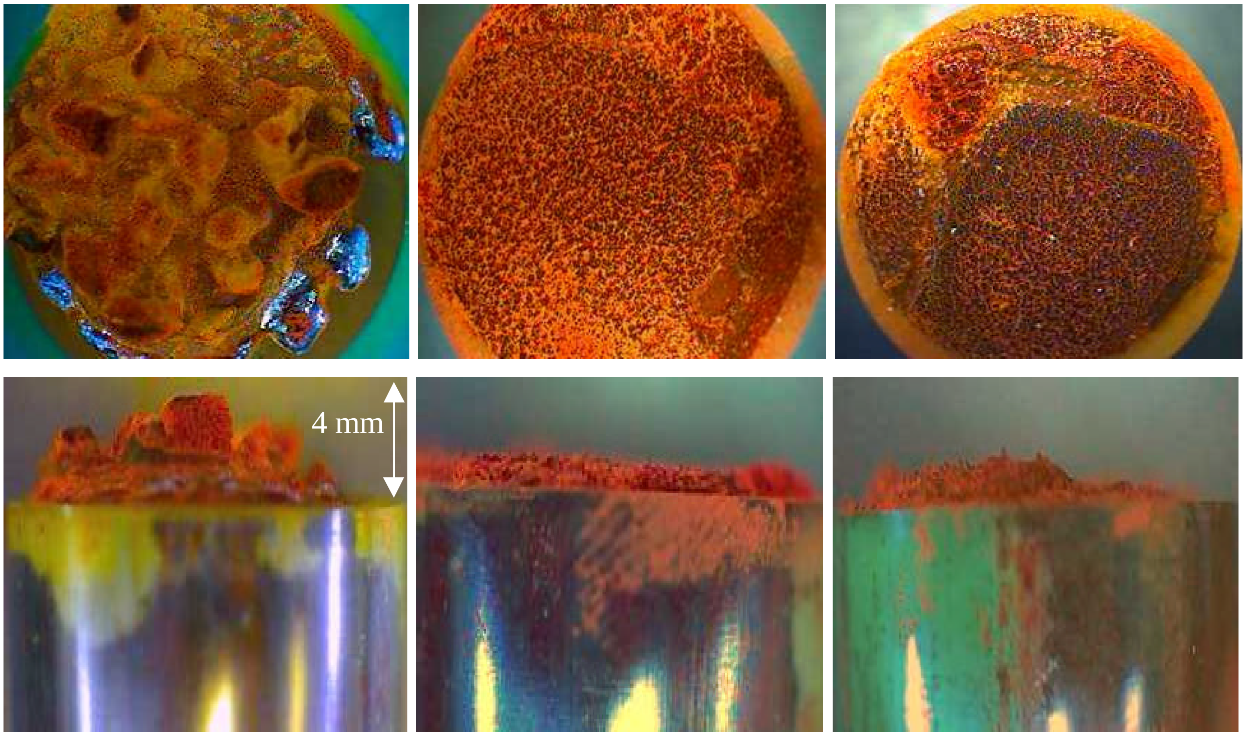


Fig 4-1: Representative total iron concentrations in water as a function of time.



5ºC 20ºC 25ºC

Figure 4-2: Iron coupons, top view (upper photos) and side view (lower photos).

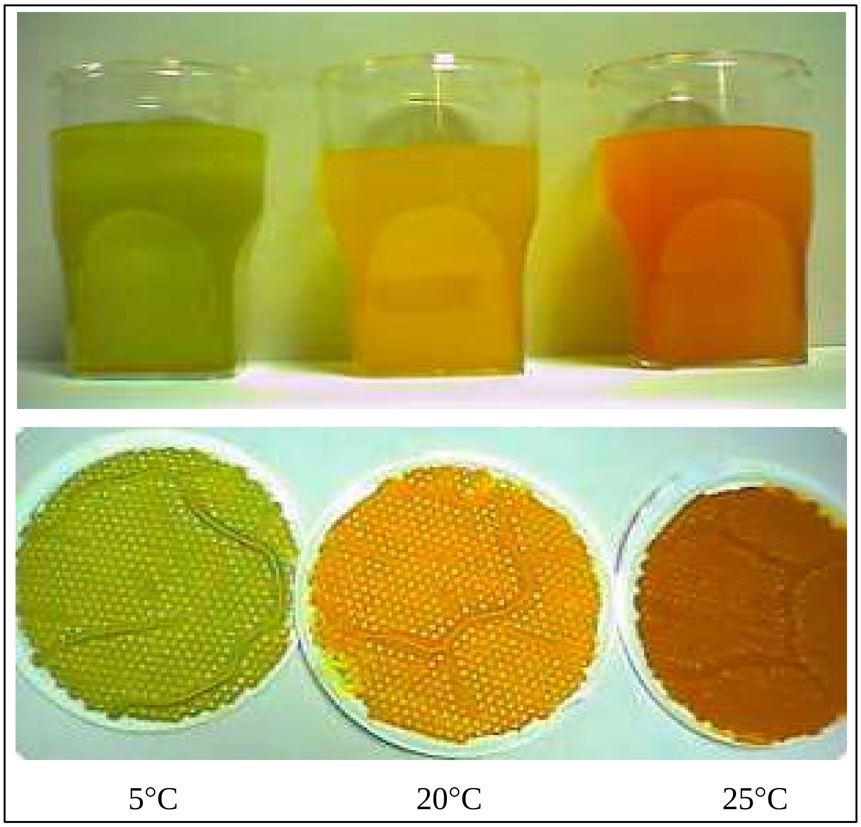


Figure 4-3: Solution after iron scale was digested (top photo) and solids retained on the filter after digestion (lower photo).

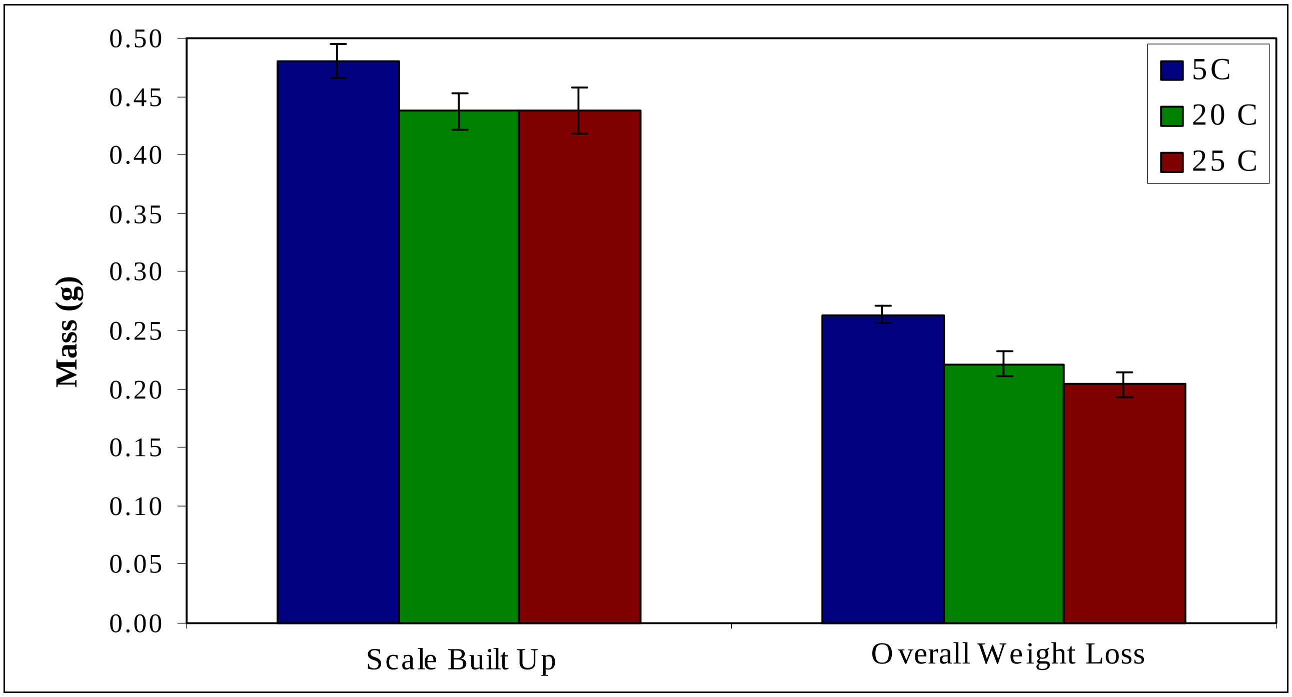


Figure 4-4: Scale build-up and overall weight loss observed after 133 days of exposure. Error bars represent 95% confidence interval based on 24 – 26 replicate samples.

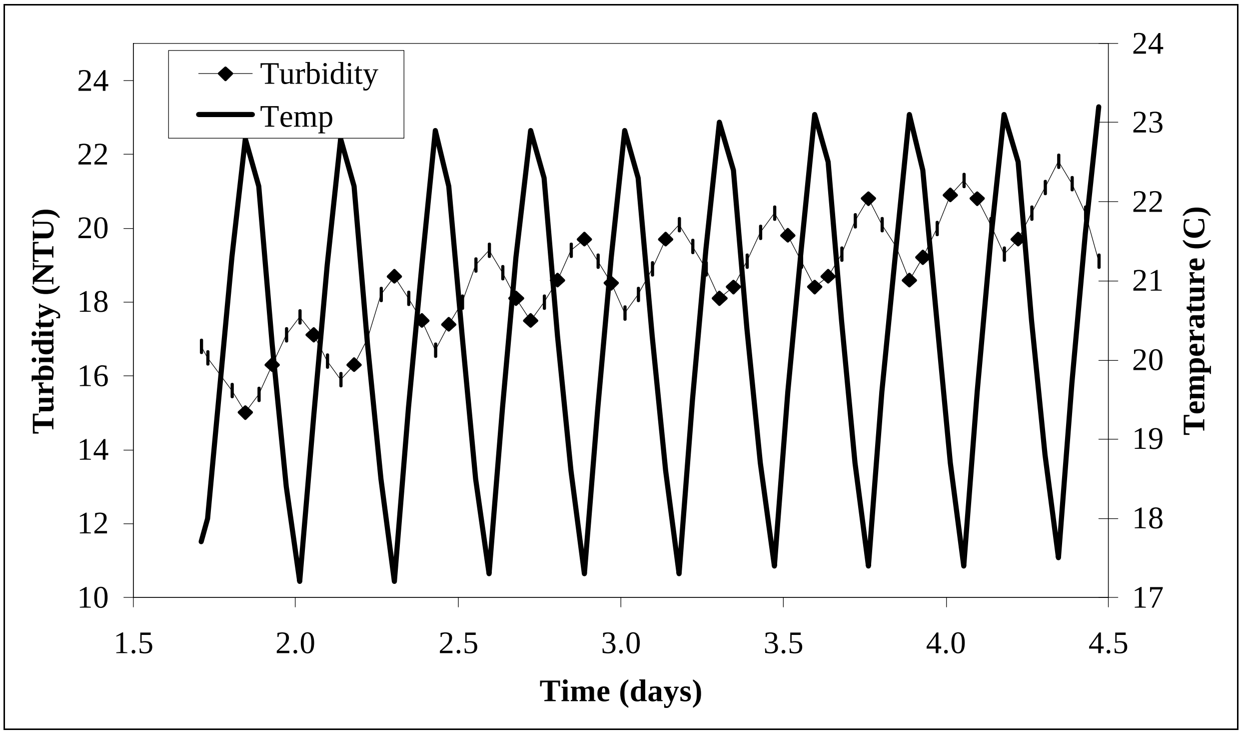


Figure 4-5: Apparent cycling of turbidity as temperature is cycled.

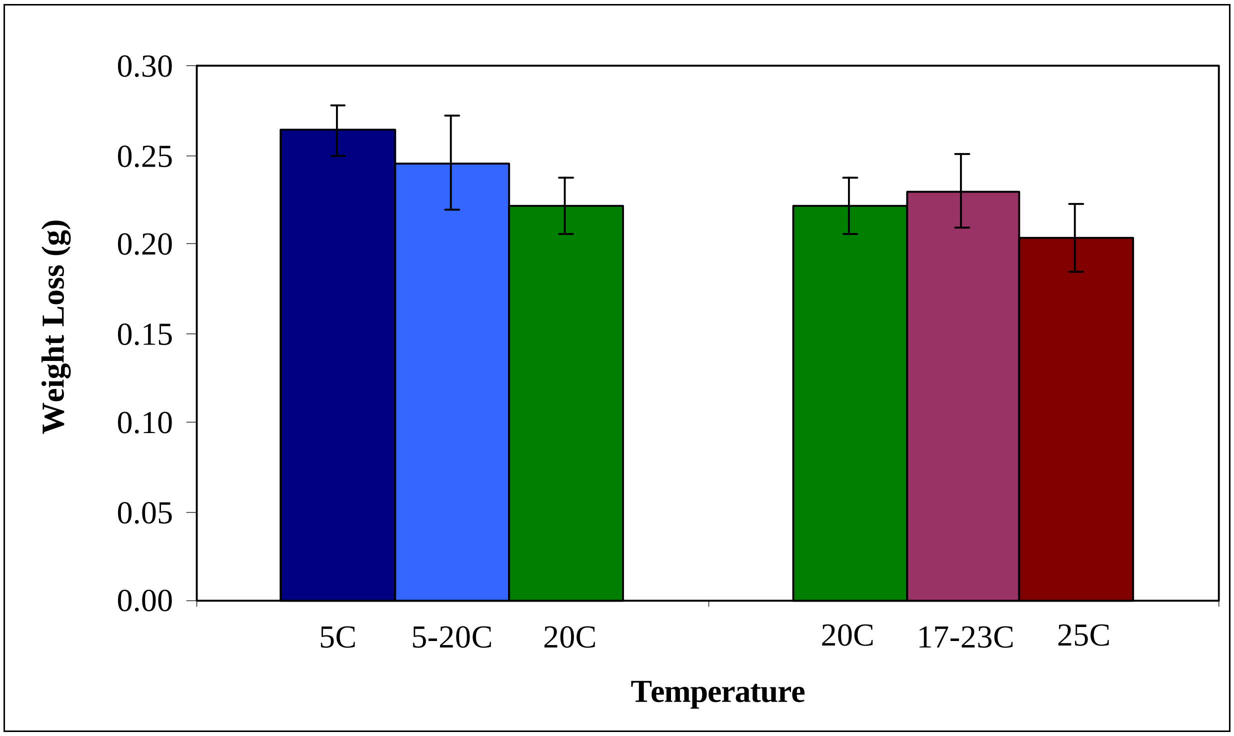


Figure 4-6: Weight loss observed after 133 days of exposure. Error bars represent 95% confidence interval based on 24 – 26 replicate samples.