INTERPLAY OF WATER CHEMISTRY AND ENTRAINED PARTICULATES IN EROSION CORROSION OF COPPER AND NONLEADED ALLOYS IN POTABLE WATER SYTEMS

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ABSTRACT

Erosion corrosion of plumbing materials in domestic water systems is a complex phenomenon driven by water quality, hydrodynamic and electrochemical factors. Erosion corrosion accounts for over a third of copper hot water system failures in the U.S., hundreds of millions in damage, and may be expected to increase with newer Legionella control strategies including increased use of water recirculation and high temperatures. Additionally, some nonleaded alloys introduced after the passage of a new federal law restricting lead content in plumbing, have been anecdotally implicated as failing prematurely from erosion corrosion compared to traditional alloys.

This dissertation includes 1) a critical review of the literature, 2) investigation of a recent rapid erosion corrosion failure in a large building plumbing system, 3) replication of this phenomena in copper and nonleaded brass in laboratory studies, and 4) evaluation of 12 nonleaded alloys against conventional leaded brass. Current plumbing codes and guidelines to prevent erosion corrosion were found to be widely inconsistent and lacking scientific evidence. Large-scale recirculating hot water pipe-loop experiments demonstrated that an aggressive hard water with entrained aragonite ($CaCO_3$) particles could cause fully penetrative failures (i.e., leaks) in brand new copper pipe and nonleaded brass fittings in just 3-49 days. This represents the first time rapid erosion corrosion failures have ever been replicated in the laboratory under conditions similar to those encountered in practice. The entrained particulates dramatically accelerated attack on metals, especially at pipe bends. In general, lowering pH, increasing flow velocity, increasing temperatures, entrainment of particles (of bigger sizes), and addition of chlorine disinfectant increased erosion corrosion rates. These results scientifically proved that hard waters are not inherently less aggressive than soft water, and in fact if $CaCO_3$ solids form they can be much more aggressive. Finally, cavitation and erosion corrosion resistance of 12 nonleaded alloys was evaluated against leaded brass; stainless steels demonstrated superior performance, silicon brass had the greatest susceptibility and remaining alloys were in the middle. This performance data can aid decision making regarding choice of alloys for various water applications.

Our work over the years, including involvement in the Flint Water Crisis, demonstrated that practicing trustworthy science as a public good requires commitment to scientific rigor, truth-seeking, managing conflicts of interest, and comprehensible evidence-based science communication. Critical problems in 21st century public science were highlighted including perverse incentives, misconduct, postmodernist “science anarchist” thought, and ineffectiveness of U.S. water utilities in communicating tap water safety to the American public.

INTERPLAY OF WATER CHEMISTRY AND ENTRAINED PARTICULATES IN EROSION CORROSION OF COPPER AND NONLEADED ALLOYS IN POTABLE WATER SYTEMS

Siddhartha Roy

GENERAL AUDIENCE ABSTRACT

Erosion corrosion, or flow-induced failures, of copper, brass and nonleaded alloys used in domestic water systems (especially, recirculating hot water systems) is a complex phenomenon driven by water quality, hydrodynamic and electrochemical factors. It can reduce the service life of copper by a factor of 10-50, accounts for over a third of copper hot water system failures in the US and potentially costs billions of dollars of damage. Moreover, newer risk management guidelines to control the pathogen Legionella pneumophila and promote water conservation in building plumbing, including increased water recirculation, hotter temperatures and higher chlorine disinfectant dose, is likely to increase rates of erosion corrosion field failures. Additionally, the 2011 Federal Reduction of Lead in Drinking Water Act came into force to protect the public from lead exposure, requiring new alloys that do not exceed a surface-weighted average of 0.25% Pb termed "nonleaded". Some of these nonleaded alloys have been anecdotally implicated as corroding much quicker than the older leaded (up to 8% lead by weight) brass that they replaced.

This dissertation presents a comprehensive literature review that summarizes seven decades of research on erosion corrosion failures, and highlights major knowledge gaps and discrepancies. Since a few landmark studies in the 1960s-70s, not much progress in understanding erosion corrosion in potable water systems has occurred in the intervening half century. Many plumbing codes and guidelines in the literature are inconsistent and are without any scientific basis. For instance, maximum velocity guidelines range from 1.5-5 ft/s for copper hot water systems, leading to considerable confusion, making it unclear how to design buildings where erosion corrosion problems are guaranteed to not occur. Multiple mechanisms, compiled under the broad term "flow-induced failures," including concentration cell corrosion, cavitation, particle/bubble impingement and high velocity impingement may play a role.

The later chapters answer many questions raised in the critical review and include a) field observations of failures in large building complex (100s of leaks in less than 48 months) and pump impellers failing in just 1.5-6 years, and b) experiments that systematically probed several water chemistry and hydrodynamic factors contributing to such failures. This dissertation represents the first ever reproduction of rapid erosion corrosion as it occurs in the field.

Bench-scale and large-scale recirculating hot water pipe-loop experiments led to identification of an aggressive hard water chemistry with entrained aragonite ($CaCO_3$) particles that caused fully penetrative pipe failures of brand new copper pipe at 8-9 ft/s,

50-55°C and pH 8 in less than one month. Entrained particulates significantly accelerated attack on metals, especially at pipe bends, and in some cases even in straight pipe sections. In general, lowering pH, increasing flow velocity, increasing temperatures, entrainment of particles (of bigger sizes), and addition of chlorine disinfectant, increased erosion corrosion rates. Subsequent experiments with newly purchased nonleaded dezincification resistant brass fittings (used with plastic PEX pipes) revealed accelerated failures (100% leaks) at 13 ft/s, 50-55°C and pH 7.5 in 3-19 days, whereas control conditions without particles had no significant damage in the same time period. These results refute decades of conventional wisdom that considered soft water as more aggressive than hard water. Moreover, if calcium carbonate precipitated as solids in water heaters or heat exchangers, the hard waters can become even more aggressive. Copper and nonleaded brass are not immune to rapid localized erosion corrosion failures, especially in the presence of particles.

Finally, in a comparative study, cavitation and erosion corrosion resistance of 12 nonleaded alloys (including brasses, bronzes, stainless steels, and newer alloy types like ECO BRASS and Federalloys) were evaluated vis-à-vis leaded red brass using an ASTM Standard Test and pipe-loop method respectively. All 12 nonleaded test alloys were more resistant to cavitation than Red Brass. Silicon Brass C87500 had the greatest susceptibility to erosion corrosion, while stainless steel alloys witnessed negligible weight loss and demonstrated superior resistance to erosion corrosion. All other alloys had erosion corrosion damage comparable to (or lesser than) the relatively stable control red brass.

In conclusion, these findings provide a basis, for ultimately improving decision making regarding choice of alloys for a variety of applications. They can also inspire future work towards continued advancement in our scientific understanding of erosion corrosion phenomena to reduce, postpone or perhaps eliminate such phenomena through improved design guidelines and water chemistry controls.

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Practicing science that is trust-worthy and as a public good, requires an aspiration to scientific rigor, truth-seeking, managing conflicts of interest, safeguards to reduce biases and logical fallacies, and evidenced based communication of results. Complementary work, inspired by years of work on events similar to the Flint Water Crisis, reviewed effective science communication strategies, and provide in-depth discussion of dangers associated with perverse incentives, ethical lapses, and rise of postmodernist engineering.

A critical review documented how incentives for academic scientists have become increasingly perverse in terms of competition for research funding, development of quantitative metrics to measure performance, and the changing business model for higher education. These factors further increased pressures on scientists as demonstrated by a conceptual model increase likelihood of unethical behavior. These incentives need to be systematically studied and addressed to minimize corruption of the scientific enterprise and resultant potential loss of public trust in science, which may have devastating

consequences to humanity. Academia and federal agencies should incentivize altruistic and ethical outcomes, while de-emphasizing output.

The second paper explored the triumph of the "citizen science" team (Flint residents, the Virginia Tech "Flint Water Study" team, and other groups) that helped uncover the Flint Lead-in-Drinking Water Crisis and led to the declaration of a federal emergency, and the later conflict between citizen scientists and "citizen engineers," who sought to disrupt engineering expertise through science anarchy. A humanitarian nonprofit, an online "news" network, a filter company and few Flint resident collaborators, practiced non-rigorous science and improper sampling that created unnecessary fear about the safety of water used for bathing and showering. These groups failed to disclose obvious financial conflicts of interest, and misrepresented/falsified data to obtain relief resources, support lawsuits, seek fame, and support testing of false scientific hypotheses. Citizen scientists must aspire to be rigorous and objective truth-seekers, whereas citizen engineers embrace subjectivity to "undermining engineering <and science> expertise" in the name of "democratizing" science and advancing their unique version of "social justice," By definition, citizen engineering is a form of "science anarchy," and our documented experiences highlight its dangers to society.

The third study examined public health communication effectiveness of water quality reports that American water utilities are federally required to provide consumers every year. These reports have potential for providing the public with accurate information on the safety of their tap water. This study evaluated the readability (or 'comprehension difficulty') of a nationally representative sample using Flesch–Kincaid readability tests. The analysis revealed that reports were written at the 11th–14th grade level, well above the recommended 6th–7th grade level and some were found to be at a level of the *Harvard Law Review* journal. These findings expose a wide gap between current water quality reports and their effectiveness for consumers.

DEDICATION

For Maa and Baba,
who gave me everything.

মা-বাবার জন্য,
জারা আমাকে সবকিছু দিয়েছে।

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"If the only prayer you ever say in your entire life is thank you, it will be enough." - Meister Eckhart

First and foremost, to my advisor and beacon of scientific brilliance and moral courage, Dr. Marc Edwards. I could not have asked for a stronger role model, mentor and guide as a 23 year old starting out in the world of water. This dissertation is an important but ultimately inadequate gauge of the enriching and productive partnership we have had and the extraordinary social impact (in Flint and nationally) we have made. Thank you Marc! I will never be able to repay all that you have done for me.

I thank my PhD committee, Drs. Bortner, Scardina and Sinha for their expertise and intellectual contributions in improving this work. Special thanks to staff in our EWR program (Beth Lucas, Betty Wingate, Bonnie Franklin, Kira Showalter, Lisa Burns, Jody Smiley, Julie Petruska, and Mary Parks), the Immigration Office, Newman Library and the Graduate School for their invaluable assistance over the years. I would like to acknowledge the financial support of the Copper Development Association, National Science Foundation, Virginia Tech's Water INTERface program, Water Research Foundation, San Jose Water Company, and Spring Point Partners.

The Edwards Research Group (also home to many on the Flint Water Study team) in Blacksburg VA has been my home away from home. I am indebted to everyone in the group, especially Jeff, Joyce, Sheldon, Min, William and Kelsey, who have taught me so much about science, civility and friendship. Credit also goes to my undergraduate student collaborators Greg, Philip, Kris, and Zihan, who were all dedicated research partners in the laboratory.

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To Amy, thank you for your love and brilliance! You make each day "very very satisfying!"

Lastly, I am grateful to my parents, Sushil and Swapna, and my sister, Sharmistha, for being perennial sources of love, mirth and succor. Maa gave me her blessing and the courage to leave all things familiar behind and fly halfway across the world. I strive to emulate her inner strength, warm-heartedness, and concern for the less fortunate every day. On a concluding note, I was little over a year old when Baba defended his PhD and dedicated his dissertation to his wife, daughter and son (me) in 1990. Twenty eight years later, I return the gesture and tip my hat to the man who was and will always be my first hero.

AUTHOR'S PREFACE

This dissertation is organized into eight chapters. Chapter 1-4 and 6-8 chapters are arranged as individual manuscripts according to Virginia Tech's specifications and are formatted based on the journal in which it was published, submitted or will be submitted to. Chapter 5 is a compilation of key intellectual contributions and conclusions from the erosion corrosion work outlined in Chapters 1-4. Each chapter manuscript was written in collaboration with Dr. Edwards (except Chapter 8) and other researchers with intellectual and laboratory contributions appropriately indicated by co-authorship. The work presented here was partially funded by the following agencies: Copper Development Association (Chapters 1 and 2), Water Research Foundation/San Jose Water Company (Chapter 4), National Science Foundation (Chapter 7), and Virginia Tech Water INTERface IGEP Program (Chapter 8).

Chapter 1 is a comprehensive literature review that summarizes seven decades of research on erosion corrosion failures, and highlights major knowledge gaps and discrepancies. Since a few landmark studies in the 1960s-70s, not much progress in understanding erosion corrosion in potable water systems has occurred in the intervening half century. Many plumbing codes and guidelines in the literature are inconsistent and are without any scientific basis. For instance, maximum velocity guidelines range from 1.5-5 ft/s for copper hot water systems, leading to considerable confusion, making it unclear how to design buildings where erosion corrosion problems are guaranteed to not occur. Multiple mechanisms, compiled under the broad term "flow-induced failures," including concentration cell corrosion, cavitation, particle/bubble impingement and high velocity impingement may play a role. This chapter is currently under review in *Corrosion Reviews* journal. Co-authors on this paper include the late Ms. Julia Novak and Mr. Jeff Coyne, former graduate research assistants in the Department of Civil and Environmental Engineering at Virginia Tech, who conducted important research that feature in this review.

Chapter 2 includes both a case study on field observations of rapid failures in large building complex (100s of leaks in less than 48 months), and experimental work where bench-scale and large-scale recirculating hot water pipe-loop experiments led to identification of an aggressive hard water chemistry with entrained aragonite ($CaCO_3$) particles that caused fully penetrative pipe failures of brand new copper pipe in weeks. Entrained particulates significantly accelerated attack on metals, especially in high turbulence areas like bends, and in some cases, in straight pipe sections. In general, lowering pH, increasing flow velocity, increasing temperatures, entrainment of particles (of bigger sizes), and addition of chlorine disinfectant, increased erosion corrosion rates. This work was the first ever reproduction of rapid erosion corrosion as it occurs in the field and will be submitted to *CORROSION* journal for publication.

Chapter 3 extends the study of Chapter 2 with experiments including newly purchased nonleaded dezincification resistant brass fittings (used with plastic PEX pipes) and revealed accelerated failures (100% leaks) of this brass at 13 ft/s, 50-55°C and pH 7.5 in

3-19 days, whereas control conditions without particles had no significant damage in the same time period. Chapters 2 and 3 proved that copper and nonleaded brass are not immune to rapid localized erosion corrosion failures, especially in the presence of particles. This chapter has been published in *Proceedings of NACE CORROSION 2016*: Roy, S. and Edwards, M.A., 2016, June. Effects of $CaCO_3$ Precipitation on Erosion-Corrosion of Non-leaded Brass Fittings in Potable Water Systems. In *CORROSION 2016*. NACE International. It will also be submitted to *CORROSION* journal for publication.

Chapter 4 is a comparative study where cavitation and erosion corrosion resistance of 12 nonleaded alloys (including brasses, bronzes, stainless steels, and newer alloy types like ECO BRASS and Federalloys) were evaluated against leaded red brass using an ASTM Standard Test and pipe-loop method respectively. All 12 nonleaded test alloys were more resistant to cavitation than Red Brass. Silicon Brass C87500 had the greatest susceptibility to erosion corrosion, while stainless steel alloys witnessed negligible weight loss and demonstrated superior resistance to erosion corrosion. All other alloys had erosion corrosion damage comparable to (or lesser than) the relatively stable control red brass. This work is part of a forthcoming Water Research Foundation report and the chapter will be submitted to *CORROSION* journal for publication. Co-authors on this paper include Mr. Philip Smith and Mr. Greg House who conducted parts of the experimental work described while working as undergraduate research assistants in the Department of Civil and Environmental Engineering at Virginia Tech.

Chapter 5 compiles key intellectual contributions, author contributions, conclusions, and recommendations for water utilities, building owners and construction companies based on original erosion corrosion research highlighted in Chapters 1-4, and also highlights recommended future work that can help further our understanding of and inform building standards and plumbing codes to reduce, postpone and perhaps even eliminate erosion corrosion cases in practice.

Chapter 6 is a critical review that documents how incentives for academic scientists have become increasingly perverse in terms of competition for research funding, development of quantitative metrics to measure performance, and the changing business model for higher education. It utilizes a conceptual model to show how these factors further increased pressures on scientists and the likelihood of unethical behavior. It calls for systematically studying these incentives and address them to minimize corruption of the scientific enterprise and resultant potential loss of public trust in science. This chapter has been published in *Environmental Engineering Science* journal: Edwards, M.A. and Roy, S., 2017. Academic research in the 21st century: Maintaining scientific integrity in a climate of perverse incentives and hypercompetition. *Environmental Engineering Science*, *34*(1), pp.51-61. DOI: https://doi.org/10.1089/ees.2016.0223

Chapter 7 explored actions of the "citizen science" team (Flint residents, the Virginia Tech "Flint Water Study" team, and other groups) that helped uncover the Flint Lead-in-Drinking Water Crisis and led to the declaration of a federal emergency, and the later conflict between citizen scientists and "citizen engineers," who sought to disrupt engineering expertise through science anarchy. A humanitarian nonprofit, an online

"news" network, a filter company and few Flint resident collaborators, practiced non-rigorous science and improper sampling that created unnecessary fear about the safety of water used for bathing and showering. These groups failed to disclose obvious financial conflicts of interest, and misrepresented/falsified data to obtain relief resources, support lawsuits, seek fame, and support testing of false scientific hypotheses. The paper shows how citizen engineering is a form of "science anarchy" and, given our documented experiences, highlights its dangers to society. This chapter is currently under review in the *Citizen Science: Theory and Practice* journal for publication.

Chapter 8 examined public health communication effectiveness of water quality reports that American water utilities are federally required to provide consumers every year. These reports have potential for providing the public with accurate information on the safety of their tap water. This study evaluated the readability (or 'comprehension difficulty') of a nationally representative sample using Flesch–Kincaid readability tests. The analysis revealed that reports were written at the 11th–14th grade level, well above the recommended 6th–7th grade level and some were found to be at a level of the *Harvard Law Review* journal. These findings expose a wide gap between current water quality reports and their effectiveness for consumers. This chapter has been published in *Journal of Water and Health*: Roy, S., Phetxumphou, K., Dietrich, A.M., Estabrooks, P.A., You, W. and Davy, B.M., 2015. An evaluation of the readability of drinking water quality reports: a national assessment. *Journal of water and health*, *13*(3), pp.645-653. DOI: https://doi.org/10.2166/wh.2015.194 Co-authors on this paper include Ms. Katherine Phetxumphou (KP; graduate research assistant in the Department of Civil and Environmental Engineering at Virginia Tech) and the following faculty at Virginia Tech: Drs. Brenda Davy (BD), Andrea Dietrich (AD), Paul Estabrooks (PE) and Wen You (WY). This dissertation's author (SR) and BD designed research; SR and KP compiled reports; SR conducted research and analyzed data; SR, BD, KP, AD, PE and WY co-authored the paper.

In addition to the eight chapters listed above, the overall body of doctoral research work includes the following publications not included in this dissertation:

- **Roy, S.**, P. Smith, G. House, and M.A. Edwards. Corrosion of Nonleaded Pump Impeller Alloys in Chlorinated Potable Water. Water Research Foundation Project 4658 Final Report. Water Research Foundation. Denver, CO, 50 pages.
- **Roy, S.**, G. House, and M.A. Edwards. Comparative Resistance of Six Copper Alloys to Erosion Corrosion in Simulated Potable Water. Final Report prepared for Chase Brass.
- **Roy, S.** and M.A. Edwards. Hard $CaCO_3$ Particles Formed by Water Heating Exacerbate Copper Erosion Corrosion. Final Report prepared for Copper Development Association.
- Phetxumphou, K., **S. Roy**, B. Davy, P. Estrabrooks, W. You and A.M. Dietrich. Assessing clarity of message communication for mandated USEPA drinking water quality reports. Journal of Water and Health, doi: 10.2166/wh.2015.134
- Lambrinidou, Y., W.J. Rhoads, **S. Roy**, E. Heaney, G. Ratajczak, J. Ratajczak. Ethnography in Engineering Ethics Education: A Pedagogy for Transformative

Listening. ASEE Annual Conference and Exposition, Jun 15-18 2014, Indianapolis, IN.

- Pieper, K.J., M. Tang, R. Martin, L. Walters, J. Parks, **S. Roy** and M.A. Edwards. Evaluating water Lead Levels during the Flint Water Crisis. Environmental Science and Technology (Submitted).
- **Roy, S.** and M. Edwards. Science is a public good in peril – here's how to fix it. Aeon Magazine. Nov 2017
- **Roy, S.** The Hand-in-Hand Spread of Mistrust and Misinformation in Flint. American Scientist. Jan-Feb 2017
- Phetxumphou, K., **S. Roy**, B.M. Davy, P. Estabrooks, W. You and A.M. Dietrich. Write Consumer Confidence Reports Customers Can Understand. OpFlow. Feb 2017

Finally, major portions of the PhD work outlined in this dissertation have been presented at the following peer-reviewed conferences:

- **Roy, S.** and M.A. Edwards. WRF 4658: Cavitation and Erosion Corrosion Resistance of Nonleaded Alloys in Chlorinated Potable Water. AWWA WQTC, Nov 12-16, 2017, Portland, OR.
- **Roy, S.** and M.A. Edwards. Cavitation and Erosion Corrosion Resistance of Nonleaded Alloys in Chlorinated Potable Water. AWWA ACE, Jun 11-14, 2017, Philadelphia, PA.
- **Roy, S.** Science for the Public Good v/s Perverse Incentives in Academia. AAAS Annual Meeting, Feb 16-20, 2017, Boston, MA.
- **Roy, S.** and M.A. Edwards. Revisiting the public health tragedy in Flint and why we are ill-equipped to prevent another. APHA Annual Meeting and Expo, Oct 29-Nov 2, 2016, Denver, CO.
- Pieper, K.J., A. Katner, **S. Roy,** and M.A. Edwards. Lead in Water Equation: Understanding variables that influence lead in drinking water. UNC Water and Health, Oct 10-14, 2016, Chapel Hill, NC.
- **Roy, S.** and M.A. Edwards. The Flint MI Water Crisis: Lessons in Communicating Science and Influencing Public Discourse with Research. AWWA ACE, Jun 19-22, 2016, Chicago, IL.
- **Roy, S.** and M.A. Edwards. Role of water hardness precipitation and flashing cavitation in erosion corrosion of copper in potable water systems. AWWA ACE, Jun 7-10, 2015, Anaheim, CA.
- **Roy, S.***, K. Phetxumphou*, A.M. Dietrich, P. Estabrooks, W. You, and B.M. Davy. Evaluating readability and clarity of USEPA mandated Drinking Water Quality Reports: A National Assessment. AWWA ACE, Jun 7-10, 2015, Anaheim, CA. * denotes equal contribution
- **Roy, S.** and M.A. Edwards. Erosion Corrosion of Copper as a function of temperature, flow rates and water hardness. AWWA ACE, Jun 8-12, 2014, Boston, MA.

TABLE OF CONTENTS

ABSTRACT ii
GENERAL AUDIENCE ABSTRACT iii
DEDICATION vi
ACKNOWLEDGEMENTS vii
AUTHOR'S PREFACE viii
LIST OF FIGURES xvi
LIST OF TABLES xx
CHAPTER 1. FLOW INDUCED FAILURE MECHANISMS OF COPPER PIPE IN POTABLE WATER SYSTEMS 1
Abstract 1
Introduction 2
Current State of the Knowledge 4
Erosion corrosion of copper and copper alloys in seawater operations 4
Theories of failure of copper tube in fresh water systems 8
Hotter temperatures, water recirculation systems and growing concerns over *Legionella pneumophila* 13
Deficiencies in reviewed theories 14
Review of Mechanisms contributing to erosion corrosion 23
Concentration Cell Corrosion 23
Cavitation Bubble Implosion and Damage 31
Particle Impingement 42
High Velocity Water Impingement 50
Summary and Conclusions 51
Acknowledgements 52
References 53
CHAPTER 2. INTERACTIVE EFFECTS OF WATER CHEMISTRY, HYDRODYNAMICS, AND PRECIPITATED CALCIUM CARBONATE HARDNESS CAUSING EROSION CORROSION OF COPPER IN HOT WATER RECIRCULATION SYSTEMS: CASE STUDY AND EXPERIMENTAL WORK 67
Abstract 67
Introduction 68
Case Study: Investigation Of Accelerated Copper Pipe Failures In A Large Building Complex 69
Finding #1: The severe erosion corrosion occurred in a system with extremely hard water (~390 ppm) 69
Finding #2: The hard water generated high concentrations of particles upon heating that clogged the plumbing system and might physically abrade copper 70
Finding #3: The cause of the failures is erosion corrosion, due to excessively high water velocity (8 ft/s), and exacerbated by the presence of abrasive particulates and/or bubbles. 71
Finding #4: Failures are not limited to the most susceptive portions of the copper pipe network downstream of valves and bends and flow constrictions,

but instead, occur with very high frequency on long straight lengths of copper tube.....73
Finding #5: Most failures were not due to either faulty installation or construction practices.....74
Finding #6: The Large and Abrasive Particles are Formed Rapidly at Higher Temperature and Pressure.....74
Review of past copper erosion corrosion failures in the geographic location surrounding Building X. 75
Experimental Procedures 76
Experiment #1: Long Term Bench Scale Jet Impingement in Hot Water Recirculation Experiments.....76
Experiment #2: Large Scale Pipe-Loop Hot Water Recirculation Experiments79
Experiment #3: Bench Scale Beaker Tests 81
Data and Analysis 83
Results and Discussion 83
Experiment #1: Long Term Bench Scale Jet Impingement in Hot Water Recirculation Experiments.....83
Experiment #2: Large Scale Pipe-Loop Hot Water Recirculation Experiments87
Experiment #3: Bench Scale Beaker Tests 94
Comparing Corrosion Rates between pipe-loop and beaker experiments.....97
Study Limitations.....98
Conclusions.....98
Future Work.....99
Acknowledgements.....99
References.....100
CHAPTER 3. EFFECTS OF $CaCO_3$ PRECIPITATION ON EROSION CORROSION OF NONLEADED BRASS IN POTABLE WATER SYSTEMS.....104
Abstract.....104
Introduction.....105
Erosion Corrosion 105
Particles and water hardness precipitation in premise plumbing.....106
Objectives of this study.....107
Experimental Procedure.....107
Pipe-loop Apparatus.....107
Water Chemistry and Test Conditions.....108
Data and Analysis 109
Results.....110
Effect of particulates.....110
Effect of pH.....111
Effect of velocity.....112
Effect of particle size 113
Effect of disinfectant type.....114
Conclusions.....115
Acknowledgements.....116
References.....116

CHAPTER 4. CAVITATION AND EROSION CORROSION RESISTANCE OF NONLEADED PUMP IMPELLER ALLOYS IN CHLORINATED POTABLE WATER 120
Abstract 120
Introduction 121
Reported failures in pump impeller operations 121
Cavitation 123
Erosion Corrosion 124
Role of Chlorine Disinfectant 125
Current research in nonleaded alloys in potable water 126
Materials and Methods 127
Test Water 127
Test Alloys 128
Cavitation Test Method 129
Erosion Corrosion Experiment 131
Results and Discussion 132
Cavitation Test 132
Erosion Corrosion Results 133
The unresolved mystery of premature impeller failures 137
Study Limitations 139
Conclusions 139
Acknowledgements 140
References 140
Supplementary Data and Figures 144
CHAPTER 5. KEY INTELLECTUAL CONTRIBUTIONS, AUTHOR CONTRIBUTIONS, CONCLUSIONS, RECOMMENDATIONS AND FUTURE RESEARCH NEEDS 149
Key Intellectual Contributions 149
Author Contributions 150
Conclusions 150
Recommendations 151
Water Utilities 151
Building Owners and Construction Companies 151
Future Work 151
References 152
CHAPTER 6. ACADEMIC RESEARCH IN THE 21ST CENTURY: MAINTAINING SCIENTIFIC INTEGRITY IN A CLIMATE OF PERVERSE INCENTIVES AND HYPERCOMPETITION 153
Abstract 153
Perverse Incentives in Research Academia: The New Normal? 154
Quantitative performance metrics: effect on individual researchers and productivity. 156
Performance metrics: effect on institutions 159
Hypercompetitive funding environments 159
Systemic Risks to Scientific Integrity 161
The high costs of research misconduct 162
If nothing is done, we will create a corrupt academic culture 164

What Kind of Profession are we Creating for the Next Generation of Academics?165
Acknowledgements....166
References....166
CHAPTER 7. HIJACKING OF CITIZEN SCIENCE BY CITIZEN ENGINEERS: LESSONS IN SCIENCE ANARCHY FROM THE FLINT WATER CRISIS....176
Abstract....176
Introduction: Origins of a Water Crisis....177
Uncovering the Flint Water Crisis with Citizen Science....177
Citizen Engineering as Science Anarchy....179
Water Defense's "Citizen Science" Program in Flint coincides with Sharp Spike in Shigellosis Cases....180
Unscientific WaterBug® testing and conflicts of interest....180
Water Defense Messaging on Bathing and Showering and Shigellosis cases in Flint....182
Collaboration between Water Defense and the Largest Online News Network in the World....185
Collaboration between Mr. Smith and promoters Of NLP Filters and Conditioners186
Citizen Science Misconduct?....187
Case 1....187
Case 2....189
Case 3....189
Sobering Lessons on Citizen Engineering and Science Anarchy from Post-Emergency Flint....191
Characteristics of Quality Citizen Science Projects....191
Post Modern Undermining of Expertise and The Dunning-Kruger Effect....193
Citizen Science with/vs Citizen Engineering: Collaborations and confrontation that are sometimes necessary but fraught with peril.....195
The Future....197
Acknowledgements....198
References....198
CHAPTER 8. AN EVALUATION OF THE READABILITY OF DRINKING WATER QUALITY REPORTS: A NATIONAL ASSESSMENT....210
Abstract....210
Introduction....211
Materials and Methods....213
Selection of CCRs....213
Assessing Readability....214
Results and Discussion....215
Conclusions....218
Acknowledgements....219
References....219

LIST OF FIGURES

1-1. Illustrative Examples of Failures that Have Been Traditionally Classified as Erosion Corrosion or Flow Induced Failures 3
1-2. Longitudinal Jet Tests for synthetic tap water and seawater at 39°C 6
1-3. Perpendicular Jet Tests for synthetic tap water and seawater at 39°C 7
1-4. Fluid-wall interactions in flow systems 23
1-5. Key Reactions on Anodic and Cathodic Regions of the Pipe Surface Produce Electron Flow through the Metal 24
1-6. Corrosion within a drop of water on iron 25
1-7. Hypothesized location of corrosion due to turbulence for iron and copper pipe 26
1-8. Simplified Schematic of Concentration Cell Pitting Corrosion for Anodically Limited Reaction 27
1-9. Simplified Schematic of Concentration Cell Pitting Corrosion for Cathodically Limited Reaction 28
1-10. Conceptualization of Macroscopic Differential Flow Patterns that naturally arise from Different Water use Patterns in Separate Branches of a Premise Plumbing System 29
1-11. Schematic of Localized High Velocity and Turbulence which may form Downstream from an Obstruction (with and without Scale Formation) 29
1-12. Simplified Schematic of Small Area (1 cm^2) of Pipe Subject to Turbulence and a Large Area (100 cm^2) of Pipe Subject to Low Velocity 31
1-13. Anodic Current Density vs. Time to Failure for Different Types and Sizes of Copper Pipe 32
1-14. Comparison of Super- and Under-saturated Cavitation Inception to Pure Vaporous Cavitation ($\sigma_{ci} = 3$) 34
1-15. Bubble collapse/implosion 36
1-16. Corrosion of Metal in Presence of an Air Bubble 37
1-17. Trapped gas in a water pipe 38
1-18. Pipe from a Real Premise Plumbing System Exhibiting Possible Cavitation Bubble Implosion Damage 39
1-19. Pressure curves for cavitation and flashing 40
1-20. Schematic showing the expansion and entrainment region of a radially flashing jet and typical temperature and velocity variation along the jet axis. 41
1-21. Pressure profile and flashing location for critical two-phase flow 42
1-22. Cyclic removal of corrosion product films by abrasion 43
1-23. Mechanisms of particle impact erosion 49
2-1. Cold water collected from Building X generated a massive amount of calcium carbonate particulate matter when heated and was visible as white turbidity 71
2-2. Every sample in a viewing area was examined and all significant internal pipe damage was caused by characteristic erosion corrosion 71
2-3. Photographs of crystals in a brass valve and in a 4" cold water blow down line 72
2-4. Very hard particulates clogged aerators with very abrasive and highly crystalline calcium carbonate particulates 73

2-5. Substantial fraction of failures occurred at bends or just downstream of valves; a very large number of failures occurred along straight sections 73
2-6. Simulated Building X water formed a soft paste when heated to either 60 °C or to 97 °C at 1 atm. pressure, but formed large hard crystals in the same test at higher temperature 75
2-7. Recirculating system schematic and test rigs built in the laboratory 77
2-8. Representative copper coupons used in Experiment #1 test rigs..... 78
2-9. Schematic of and photos of pipe-loop apparatus for copper erosion corrosion testing..... 79
2-10. Representative aragonite particles used in experiments alongside particles founding in Building X's plumbing 81
2-11. Bench Scale Beaker Experiment Schematic and Representative Example in the laboratory 82
2-12. Copper release rates for four conditions of 'Phase-I' experimentation (Building X Hard and Soft Waters at 70 °C and 48 °C) at 25 ft/s. 84
2-13. Total Copper release for four conditions of 'Phase-I' experimentation (Building X Hard and Soft Waters at 70 °C and 48 °C) over 48 days. 84
2-14. Thickness losses in Type M 5/8" copper coupons with NOM (and Ammonia + Nitrate added 66 days after experiment started). 86
2-15. Progression of non-uniform erosion corrosion patterns in Hard-NOM-65°C condition (Day 0, Day 130, Day 160, and Day 204). 86
2-16. Wall thinning of copper specimens after 85 days in pH 7, NOM, and 25 ft/s Building X water with specific additives and respective % Wall thickness loss..... 87
2-17. Fully penetrating leak in pipe in system with small aragonite particles and close-up of leak..... 88
2-18. Time to failure for 10 ft x 10 ft pipe-loop conditions and close-up photos of elbow damage 89
2-19. New impeller compared to damaged impeller in system with large particles, representative hole in plastic pump housing. 89
2-20. Time to failure for 4 ft x 5 ft pipe-loop conditions and close-up photos of elbow damage for aragonite particle conditions and pH 7.5 and pH 10.0..... 90
2-21. Damage in long straight runs for the 'Large Particles' condition 91
2-22 Representative photos of top sections of no particles v/s Large Particles and ESEM images of their microsurface at 5000X magnification..... 91
2-23. Magnified images (53X) along the bottom of the top pipe segment for the 'Small Particles' condition. 92
2-24. ESEM images of the bottom section of horizontal pipes at 5000X mag to compare damage patterns for control, small particles and large particles. 92
2-25. Close-up photos of erosion corrosion in ambient dissolved oxygen condition and low dissolved oxygen condition..... 94
2-26. Abrasion mechanism strictly dependent on aragonite particles attacking metal and rust layer, erosion corrosion mechanism where particle impingement mechanistically removes metal/scale and electrochemical reactions (corrosion) of underlying metal occurs..... 94
2-27. Weight loss of copper wires in beaker tests for aragonite and calcite particles at 48 °C and 60 °C 95

2-28. Close-up photos of copper wires showing worst erosion corrosion attack for control, calcite and aragonite particles 95
2-29. Weight loss of copper wires in beaker tests with different particle sizes 96
2-30. Close-up photos of copper wires showing worst erosion corrosion attack w.r.t. increase in particle size 96
2-31. Weight loss of copper wires in beaker tests w.r.t. different disinfectants 97
2-32. Close-up photos of copper wires showing worst erosion corrosion attack w.r.t. various disinfectants 97
3-1. Representative particulates used in tests alongside those from a real system 106
3-2. Schematic of pipe-loop apparatus for erosion corrosion testing of nonleaded brass 109
3-3[a]. Side-by-side comparison of fresh brass with tested conditions of 'Control' and 'Large particles' at pH 7.5 & 10 110
3-3[b]. ESEM images of no particles and large particles conditions both at pH 7.5 (at 100x) 111
3-4. Time to failure of brass elbows at pH 7.5 & 10 due to erosion corrosion 112
3-5[a]. Max. thickness loss in nonleaded brass at high and low velocities after 13.5 days 113
3-5[b]. Horseshoe-shaped erosion corrosion patterns at low velocity condition 113
3-6[a]. Maximum Thickness loss in nonleaded brass witnessed with small & large particles after 13.5 days 114
3-6[b]. Erosion corrosion patterns with small particles 114
3-7[a]. Time to failure for nonleaded brass failures without and with disinfectants 114
3-7[b]. Side-by-side comparison of tested brass pieces 114
3-8 [a-c]. ESEM images (200X mag) of tests with no disinfectant, chlorine & chloramine 115
4-1. Pump impeller section that witnessed extensive short-term damage while in service 122
4-2. Illustrative cavitation types occurring in pump impeller operations 123
4-3. Rapid failures in nonleaded brass fittings from a commercial vendor 125
4-4. Illustrative alloy specimens used in cavitation and erosion corrosion experiments 129
4-5. Modified ASTM G32-10 cavitation apparatus setup 130
4-6. Eroded tips of cavitation horn 130
4-7. Erosion corrosion apparatus schematic and constructed pipe rig setup 131
4-8. Reinforcements used to make alloy location elbow-PEX pipe joint leak-tight. 131
4-9. Averaged percentage weight loss for cavitation tests 132
4-10. Visual comparison of worst cavitation damage to thirteen copper alloys 133
4-11. Average percentage weight loss for thirteen copper alloys subjected to erosion corrosion pipe loop testing 133
4-12. Box-and-whiskers plot of percentage weight loss for thirteen copper alloys subjected to erosion corrosion pipe loop testing 134
4-13. Worst case % weight loss for thirteen copper alloys subjected to erosion corrosion pipe loop testing 135
4-14. Visual comparison of erosion corrosion damage to thirteen copper alloys. 136
4-15. Microstructure of alloy surfaces subjected to erosion corrosion testing through ESEM 137
A.1. Distribution of weight loss data by orientation per alloy 148
6-1. True scientific productivity vis-à-vis emphasis on research quality/quantity 157
6-2. Trends in research intensity (i.e., ratio of U.S. R&D to gross domestic product), roles of federal, business, and other nonfederal funding for R&D: 1953–2013 160

7-1. Shigellosis cases in Flint (2012-15 v/s 2016) vis-à-vis public statements by Water Defense and other agencies on bathing, showering and shigella made on local, national or social media 183
7-2. Resident A's lead levels during the Flint Water Crisis. 188
7-3. Lead levels for water samples obtained from Resident B through all five rounds of citizen testing. 189
7-4. Resident C's lead levels during and after the Flint Water Crisis 2016-17 190
7-5. The Dunning-Kruger Effect..... 195
7-6. The Scientific Goal v/s The Activist Goal – A conceptual framework of when interests align and when they do not, with real world examples from the Flint Water Crisis 197
8-1. Map of US EPA regions and the states in which the selected CCRs are located..... 213
8-2. Box plot showing the reading ease range of 30 CCRs 216
8-3. Box plot showing the grade level range of 30 CCRs 216

LIST OF TABLES

1-1. Summary of erosion corrosion damage mechanisms 11
1-2. Velocity-Temperature recommendations to prevent erosion corrosion in copper tubing 16
1-3. Factors besides velocity and temperature contributing to erosion corrosion 18
1-4. Experimental techniques used to study erosion corrosion in various fluid conditions 21
1-5. Simplified Example of Expected Failure Time among Concentration Cell Reactions Controlled Anodically and Cathodically for New ¾" Type M Copper Tube..... 31
1-6. Comparison of classical Vaporous and Gaseous Cavitation 35
1-7. Miller numbers for various samples of a copper ore 47
2-1. Building X water chemistry..... 76
2-2. Test conditions for bench-scale recirculation experiments 78
2-3. Experimental conditions evaluated using 10 ft x 10 ft copper recirculation rigs 79
2-4. Experimental conditions evaluated using 4 ft x 5 ft copper recirculation rigs 79
2-5. Final hard water chemistry "recipe" determined to cause erosion corrosion and utilized in lab scale pipe-loop experiments for copper 80
2-7. Experimental conditions evaluated using short-term beaker experiments 82
2-8. Corrosion rates of experiments with suspended aragonite particulates at pH 7.5 and water temperature range of 50°C-60°C 98
3-1. Summary of experimental conditions in this study 108
3-2. Chemistry of the test water for erosion corrosion experimentation 109
4-1. Summary of premature failures of nonleaded brass impellers 122
4-2. Summary of research findings on nonleaded brasses in the last decade 126
4-3. Test water quality parameters..... 127
4-4. Project test alloys..... 128
4-5. Chemical composition of test alloy and damaged pump impeller measured using XRF and ICP-MS..... 138
A.1. Test alloys and constituent major elements 144
A.2. Summary Statistics for cavitation experiments..... 145
A.3. Summary Statistics for erosion corrosion experiments..... 145
A.4. ANOVA Table for erosion Corrosion results 145
A.5. Holm-Bonferroni Sequential Correction Calculations for erosion corrosion results..... 146
A.6. ANOVA Table for erosion corrosion results by orientation..... 147
6-1. Growing Perverse Incentives in Academia 155
7-1. Strategies from Freitag and colleagues (2016) used to assess the initial Virginia Tech-Flint residents "citizen science" collaboration and Water Defense-TYT Politics "citizen engineering" practices 192
8-1. Analysis of readability of adult reading materials..... 215

CHAPTER 1. FLOW INDUCED FAILURE MECHANISMS OF COPPER PIPE IN POTABLE WATER SYSTEMS

Siddhartha Roy, Jeffrey M. Coyne, Julia A. Novak and Marc A. Edwards

ABSTRACT

Erosion or velocity-induced copper pipe corrosion is a significant problem in potable water systems and especially hot water recirculation systems. The little scientific work done in freshwater has not always been able to scientifically isolate the key factors causing these failures; in fact, most existing recommendations rely on anecdotal and/or experiential knowledge from forensic analysis of field failures, which are not confirmed by complementary laboratory research. Consequently, this comprehensive review summarizes prior observations that include mechanical and electrochemical attack induced by water chemistry, temperature, velocity, hydrodynamic conditions, presence of particulate matter, and other variables thought to influence/exacerbate erosion corrosion. Distinct phenomena thought to contribute to erosion corrosion or 'flow induced failure' including concentration cell corrosion, cavitation, particle/bubble impingement and high velocity impingement are explored in detail, along with conventional erosion corrosion testing methods. Existing recommendations to prevent erosion corrosion in copper pipes are evaluated and inconsistencies in available guidelines are examined.

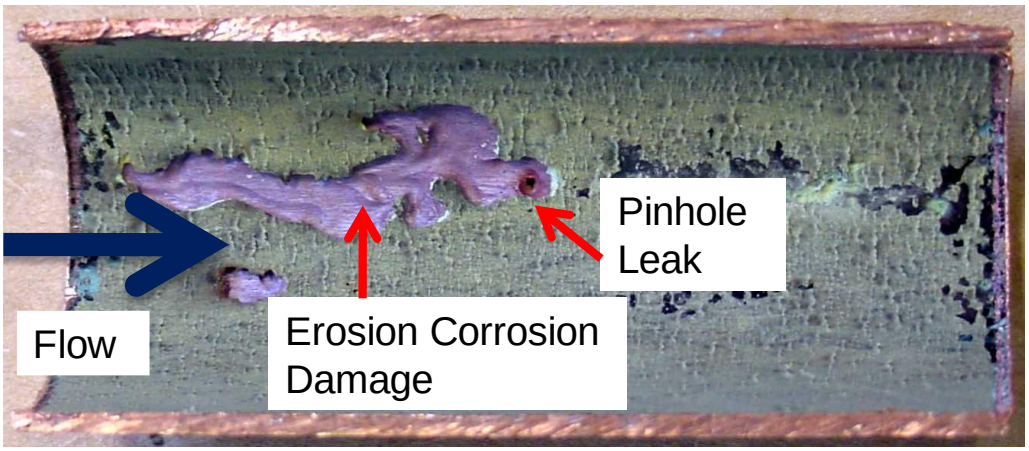
KEYWORDS: copper pipe, erosion corrosion, flow-induced failure, potable water, premise plumbing

INTRODUCTION

Copper pipes have been used for domestic water service since the dawn of civilization (Rambow and Holmgren Jr. 1966) and are a dominant material for domestic plumbing systems in Europe, North America, Australasia amongst others. The annual world production of copper water tubing is ~ 500,000 tons which is equivalent to about 1.25 million kms of pipe (Sequeira 2011). Since World War II, over 18 billion pounds (or, 8.2 billion kilograms) of copper plumbing tube has been produced in the United States alone, 80% of which has been installed in water distribution systems. This translates into more than 11.26 million kms of copper tube (CDA 2016). The net value of copper potable water infrastructure in buildings throughout the United States alone is on the order of 0.5 – 1 trillion US dollars (Edwards and Michel 2013).

Hock et al. (1994) suggested that copper potable water piping systems have a service life of 100 years in non-aggressive waters, Lewis (1999) underscored that a conservative 20-year service life could be used for design purposes, while 25-30 years or more is obtained in many areas of the US. In fact, the Copper Development Association (CDA) warrantees 50 years of service life in non-corrosive waters (2010). The high levels of quality control exercised in modern tube producing plants coupled with copper's excellent corrosion resistance give manufacturing related failure rates of less than one in a million. (Sequeira 2011). However, incidences of short term failures of copper tube have been reported in the literature (Myers and Obrecht 1973, NACE 1980, Sumitomo 1994, During 1997, Villalobos 2007, Roberts 2007, Scardina et al. 2008, Sarver et. al 2011, Gates 2012; Lytle et al. 2012) and about 8% of homeowners in the US have experienced at least one pinhole leak (Scardina et al. 2008).

Copper plumbing materials can corrode and fail from a variety of mechanisms. This review focuses on rapid failures of copper-based plumbing materials in potable water systems due to *erosion or velocity-induced corrosion*. In classic erosion corrosion failures, the attacked metallic surface gives an appearance of having been swept clean, or eroded away, presumably by localized hydraulic turbulence (Figure 1-1).



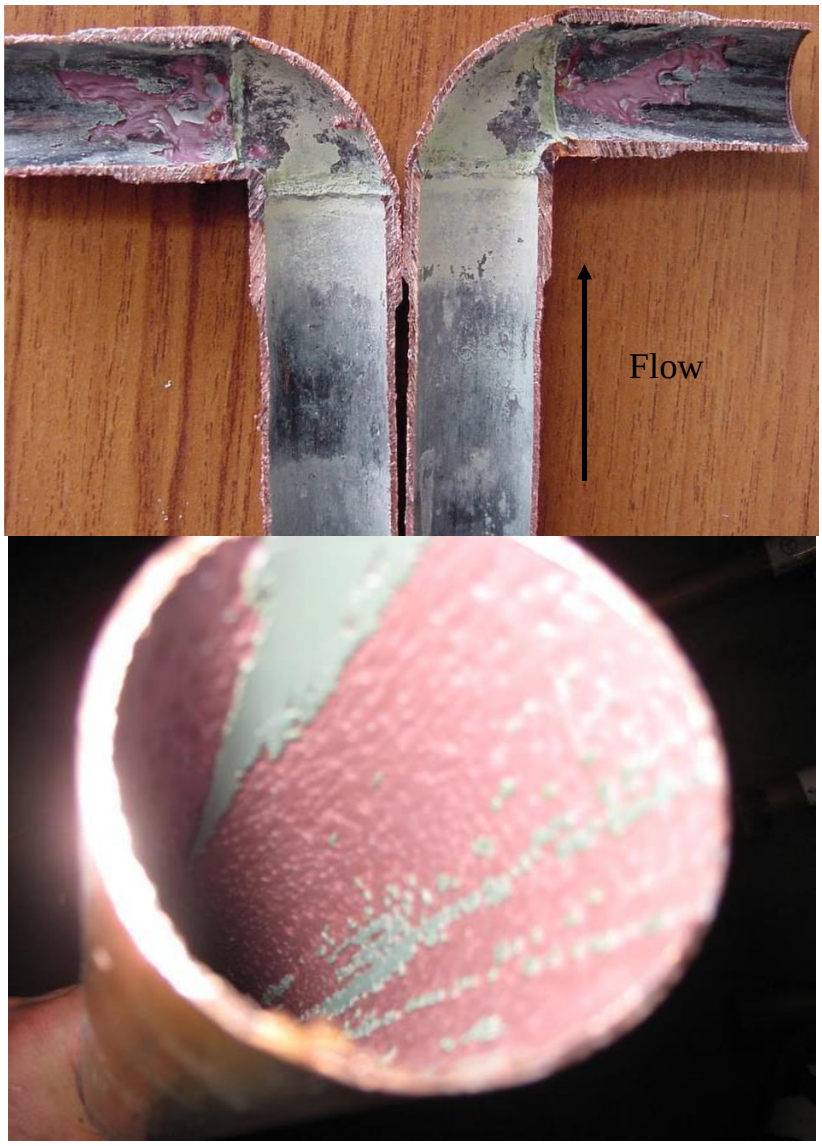


Figure 1-1. Illustrative Examples of Failures that Have Been Traditionally Classified as Erosion Corrosion or Flow Induced Failures

Areas of pipe surface affected by erosion corrosion are typically bright, shiny and with minimal copper rusts or other deposits. There is significant reduction in wall thickness in areas undergoing attack (Scardina et al., 2008), and pinhole leaks tend to occur in areas with wavelet type or horseshoe-shaped pits whose open ends face downstream of water flow direction (Campbell 1982, Cohen 1993) resembling tracks of a "horse walking upstream" (Oliphant 2010). They can also be characterized in appearance by deep grooves, gullies, waves, rounded holes and valleys (Myers and Obrecht 1972, Singley et al. 1984). Sometimes the attack is so severe that the entire surface is rough, and the characteristic horseshoe pits are not clearly seen but thinning of the tube wall becomes evident (CCBDA 1997).

While many factors have been hypothesized to contribute to erosion corrosion, there has been little fundamental progress in the laboratory replicating the phenomena as it occurs in the field, and as a result systematic studies examining causal factor(s) are lacking. Syrett emphasized an

"urgent need for a new approach to erosion corrosion studies" over 40 years ago (1976), but progress has been limited.

In the meantime, sustainability goals of promoting water conservation and energy efficiency in modern construction, especially "green" buildings, have resulted in increased adoption of hot water recirculation, higher water temperatures (up to 60°C) and building point-of-entry chlorine dosing to control growth and proliferation of opportunistic pathogens like *Legionella pneumophila* (ASHRAE 2015). Unfortunately, implementation of similar practices under the AS/NZS 3500-4 standard in Australia and New Zealand led to an alarming rise in erosion corrosion failures of copper in hot water recirculation systems (Nicholas and Gates 2012), and there is an expectation that a similar wave of failures (i.e. unpredictable and premature leaks, widespread damage to water infrastructure and associated economic losses) could occur elsewhere.

Similarly, passage of the 2011 Federal Reduction of Lead in Drinking Water Act lowered the allowable lead content of metal alloys (often, copper-based like brass) used in potable water systems from up to 8% to less than 0.25% starting January 2014 (SDWA 2011). This has led to newer nonleaded alloys flooding the market, which have not undergone rigorous long-term testing for erosion corrosion resistance-- anecdotal reports suggest at least some of these alloys are failing prematurely in the field due to erosion corrosion (Devries 2014).

This review is aimed at summarizing the present state of knowledge, critique current (and sometimes conflicting) recommendations in the literature and identify high-priority research gaps that need the industry's attention.

CURRENT STATE OF THE KNOWLEDGE

Erosion corrosion of copper and copper alloys in seawater operations

There has been many revelatory studies into erosion corrosion of copper and copper alloys caused by flowing seawater (Campbell and Carter 1961-62, Danek 1966, Yandushkin and Korkosh 1970, Ferrara and Gudas 1972, Syrett 1976, Efird 1977, Bianchi et al. 1978, Birn 1984, Heider and Bohm 1988, Wojcik 1997, Lenard 1998, Schleich 2004, Kocicin et al. 2008, Coyne 2009). Bianchi and colleagues describe "horse shoe corrosion" caused by rapid localized attack on the surface, where the seawater pH is a determining factor and corrosion is heavily influenced by local hydrodynamic conditions and turbulence (1978). Seawater is very prone to rapid erosion corrosion, due to a) very high chloride ion activity – seawater chloride concentrations on average are ~77X higher than EPA maximum secondary drinking water standards – that destroys the protective film, and b) dissolved oxygen that can both promote oxide layer growth and accelerate corrosion depending on the conditions (Danek 1966, Johnson 2007). In jet-impingement studies with seawater involving bubbly flow (controlled bubble size between 1.0-2.3 mm) on high tensile brass (~60% Cu) at 30 ft/s, the rate of wall penetration increased compared to bubble-free jet conditions due to mechanical action of the bubbles. Sustained periods of turbulent attack can eventually overwhelm relatively protective films, leading to rapid material loss (Campbell and Carter 1961-62).

Without a protective scale in place, the water can directly attack the underlying metal/alloy surface. Danek (1966) tested 56 alloys with seawater at velocities up to 120 ft/s (or 36.6 m/s) and found that copper alloys exhibit excellent corrosion resistance at low velocities (<2 ft/s or 0.6 m/s). They are, however, subject to degradation by erosion corrosion at intermediate to high velocities (>15 ft/s or 4.6 m/s) thought to strip away protective oxide films. This hypothesis is further supported by the observation that copper alloyed with elements like iron, aluminum, and chromium are more resistant to erosion corrosion (Syrett 1976), making them more suitable for condenser tubes in ocean-going ships or in power stations using tidal water than pure copper (Sequeira 2011).

For copper and its alloys, increasing flow velocity often has no significant effect on corrosion rate until a "critical" or "breakaway" velocity (possibly a "critical shear stress") has been reached (BS MA 1973). The acceptable maximum design velocity for copper in seawater, as per the American Society of Metals' Metals Handbook, is 0.6-0.9 m/s (or, 2-3 ft/s) (ASM 1987). An abrupt increase in corrosion rate past the critical velocity occurs once the scale is destroyed and its protectiveness is lost; the corrosion rate then becomes purely mass transport controlled according to boundary conditions of a scale-free system (Schmitt and Bakalli 2010). The exposed base copper surface then acts as an anode while the surrounding oxide layer is the macro-cathode, which further increases the corrosion rate until the oxide layer is completely separated and the rate then plateaus (Matsumura, 2012). Coyne (2009) performed longitudinal and perpendicular water impingement tests (Figures 1-2 and 1-3) on 0.032" (or 0.813 mm) thick copper plates (similar to a Type M ¾" copper pipe wall) using both synthetic sea and tap waters at 39°C. While the seawater caused significant damage within 4 weeks, no damage was observed in identical parallel tests with potable water (Figure 1-3). The profound differences in rate of attack in seawater versus freshwater, has been attributed to the aggressiveness of the former (specifically, salinity/chloride levels and sulfide pollution), in conjunction with high flowrates, temperature and oxygen content of the water (Danek 1966, Sequeira 2011). Despite some similarities, the erosion corrosion studies in seawater may not be directly translatable to potable water systems.

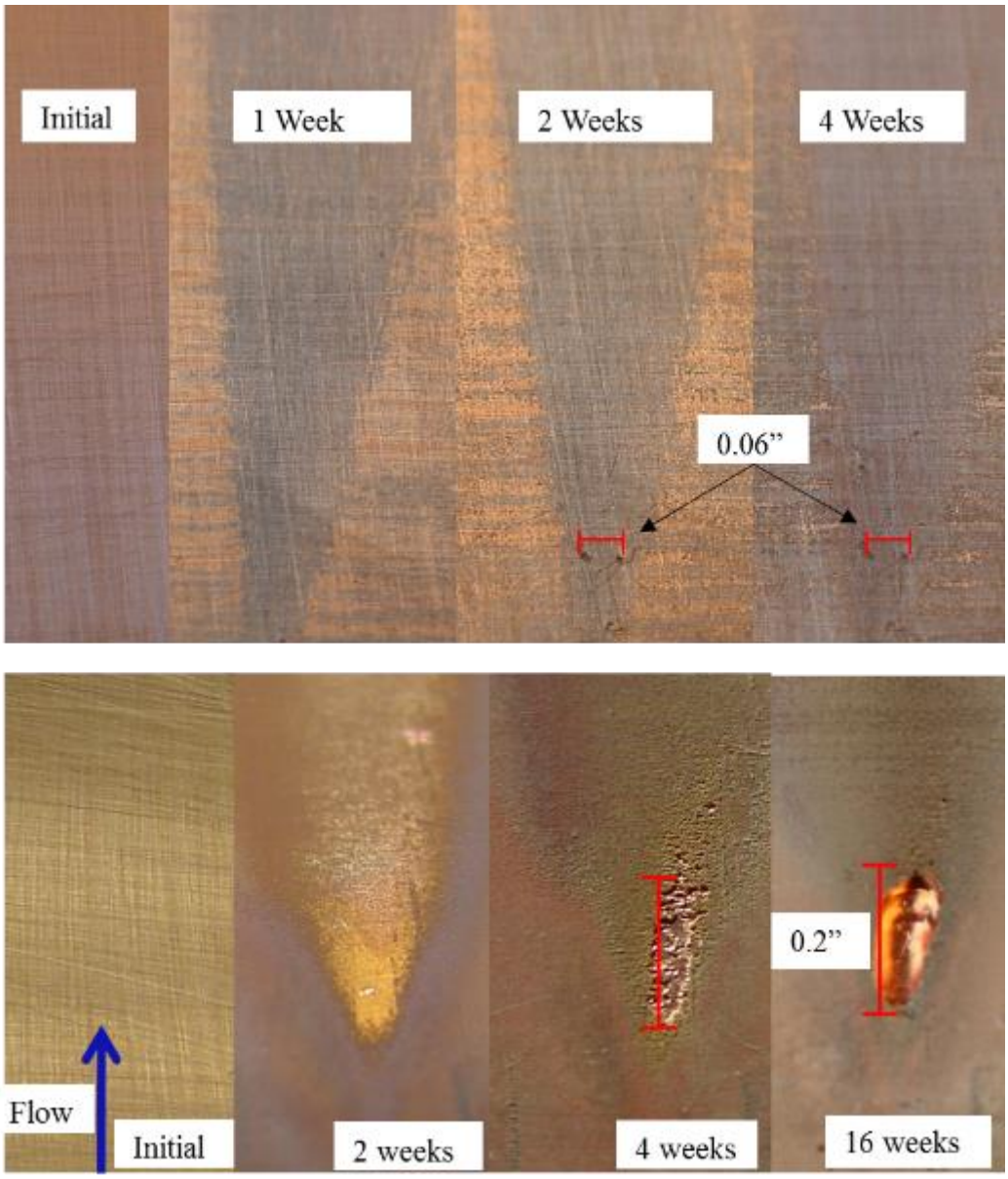


Figure 1-2. Longitudinal Jet Tests from Coyne (2009) for synthetic tap water (top) and seawater (bottom) at 39°C

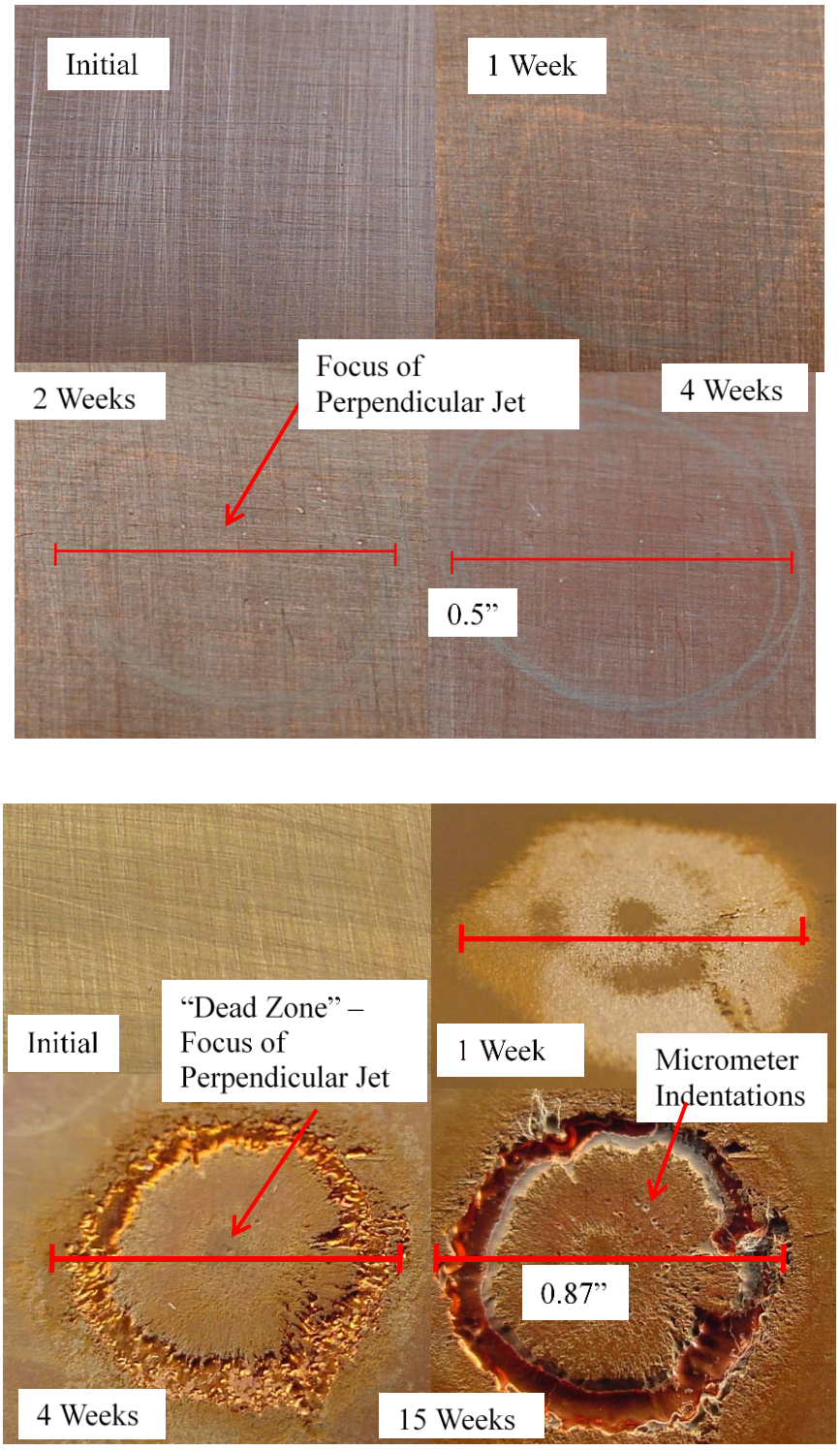


Figure 1-3. Perpendicular Jet Tests from Coyne (2009) for synthetic tap water (top) and seawater (bottom) at 39°C

Theories of failure of copper tube in fresh water systems

Erosion corrosion in freshwater has been described as a localized wearing-away of pipe material due to rapidly flowing corrosive liquid (Knutsson et al. 1972) or accelerated localized attack due to high surface shear stresses (Roberge 2004, Myers and Cohen 2005). Syrett (1976) asserts that erosion corrosion is the difference in attack rate on metal when exposed to a flowing "corrodent" (sic) as opposed to that occurring in stagnant conditions.

A mechanism analogous to that for seawater was described by Obrecht and Quill (1960a-f; 1961) and Murakami et al. (2003), who indicated that erosion corrosion mechanistically removes protective surface films (or, scales) that leaves bare copper metal fully exposed to the corrosiveness of the bulk water. The satisfactory performance of copper in potable water is critically dependent on the presence of protective films including cuprous oxide Cu_2O (formed by anodic oxidation usually under dynamical flow) and basic copper carbonates and other materials (formed from waters containing carbon dioxide and oxygen). If these films are absent, copper will fail rapidly from corrosion (Edwards et al., 1994; Sequeira, 2011). It is believed that there are, therefore, two major processes contributing (often, in synergy) to erosion corrosion: a) mechanical, comprising of physical/hydrodynamic factors including flow rates, cavitation, gas bubble and particulate impingement, and b) electrochemical and/or chemical, where water chemistry, temperature and corrosion reactions dictate material loss. This synergism is sometimes expressed in erosion corrosion literature by the following theoretical equation:

$$S = T - (E + C) \qquad \text{(Equation 1-1)}$$

where, S is the synergistic overall rate, T is the total erosion corrosion rate, E is erosion-only material loss rate and C is the corrosion-only material loss rate (Burson-Thomas and Wood, 2017). Hence, if the actual wall penetration rate is 10 mpy, and 1 mpy would be lost due to erosion alone (i.e., measured without an oxidant such as O_2 present) and 1 mpy would be lost due to corrosion, the synergy is 8 mpy. Wood and Hutton's approach of plotting data from prior experiments conducted to obtain pure erosion (E), pure corrosion (C) and combined (T) rates as log-log S/C vs. E/C graphs are enlightening to illustrate synergistic mechanisms (1990), even though the non-standard and imprecise nature of the experimental techniques themselves (see Table – 1-4 for illustrative examples) can make the approach extremely difficult to apply in practice.

Bengough and May (1924) thought that high velocity jets impinging against copper specimens not only prevented the protective surface scale from forming but also accelerated the corrosion rate, perhaps due to unusual flow characteristics in the direct vicinity of the pipe wall (Schmitt and Bakalli 2010). Knutsson et al. (1972) indicated that copper pipe loops exposed to intermittent flow ($\leq$ 25% of the time) showed no erosion corrosion as opposed to severe damage in constant flow at the same velocity, suggesting that the removal of protective scale layers takes time (Syrett 1976).

Bengough and May hypothesized that the jets also caused separation of the anodic and cathodic regions of the copper, driving accelerated localized corrosion reactions via formation of a concentration cell (1924). Coyne et al. examined this hypothesis explicitly and found that copper

surfaces exposed to high flow were, indeed, extremely anodic in certain situations and subject to very high (> 60 $\mu A/cm^2$) corrosion rates; the protective scale, however, was not removed in normal potable water chemistries even at water velocities greater than 7 m/s or 23 ft/s (2009).
Gas bubble cavitation (Obrecht and Quill, 1960f; Myers and Obrecht, 1972; US ACE 1995; Sakamoto et al., 1995, Novak, 2005) and solid particles impacting or impinging (Knutsson et al., 1972; Cohen and Lyman, 1972) against the copper pipe surface have been identified as factors initiating or exacerbating erosion corrosion in certain circumstances. Myers and Obrecht (1972) noted that suspended solids can be abrasive and can accelerate erosion corrosion in rapidly moving waters.

Cuprosolvent waters and waters softened to near zero hardness have also been suspected of contributing to erosion corrosion (NACE 1980, US ACE 1995, Oliphant 2010). Hard waters were once believed non-corrosive, because of possible formation of protective calcium compounds on the inner pipe surfaces, although the presence of such solids have not been observed or validated in the laboratory. Sequeira states that "the (corrosion) rate in an aggressive supply water may be as high as 0.26 mm/year" (sic) and that these waters can be corrosive enough to pick up sufficient copper to form green stains on plumbing fixtures (2011). To reduce this perceived aggressiveness, naturally soft waters are usually stabilized or conditioned by increasing alkalinity and/or adding corrosion inhibitors like phosphates (WHO 2011). It has also been asserted that when waters with temporary hardness are softened, they can become aggressive if heated above 140 °C due to precipitation of the $CaCO_3$ and breakdown of the bicarbonates resulting in an increase in CO_2 (i.e., a decrease in pH) (Sequeira 2011).

Obrecht and Quill (1960e) tested copper pipes of various diameters (0.95-31.75 mm) yielding different velocities (1.5-13.1 ft/s or 0.45-4 m/s) for the same flow rate (22.7 liters/minute) at temperatures 10°C – 93.3°C in recirculating loop experiments for about 1.5 years. For conditions of (sodium zeolite) softened waters and two blended waters (60 mg/L and 110 mg/L both as $CaCO_3$), they found that soft waters at pH 7.0 and medium alkalinity contribute to erosion corrosion when the water temperature is greater than 45°C and observed maximum corrosion near 77°C. They theorized that this temperature effect could be due to an increase in copper dissolution, diffusion rates and electrical conductivities, which may speed up corrosion. When the water hardness was increased to 110 mg/L (as $CaCO_3$), maximum corrosion was observed at 60°C instead of 77°C.

Kristiansen (1977) also found that copper corrosion was exacerbated at high temperatures in low alkalinity waters between pH 5.6 and 6.1 during continuous flow operation. That three-month test illustrated water containing natural organic matter (NOM) further accelerates the corrosion rate with increasing temperature. He reasoned that the organic matter might prevent the formation of a black, protective copper oxide film that often forms in hot water systems.

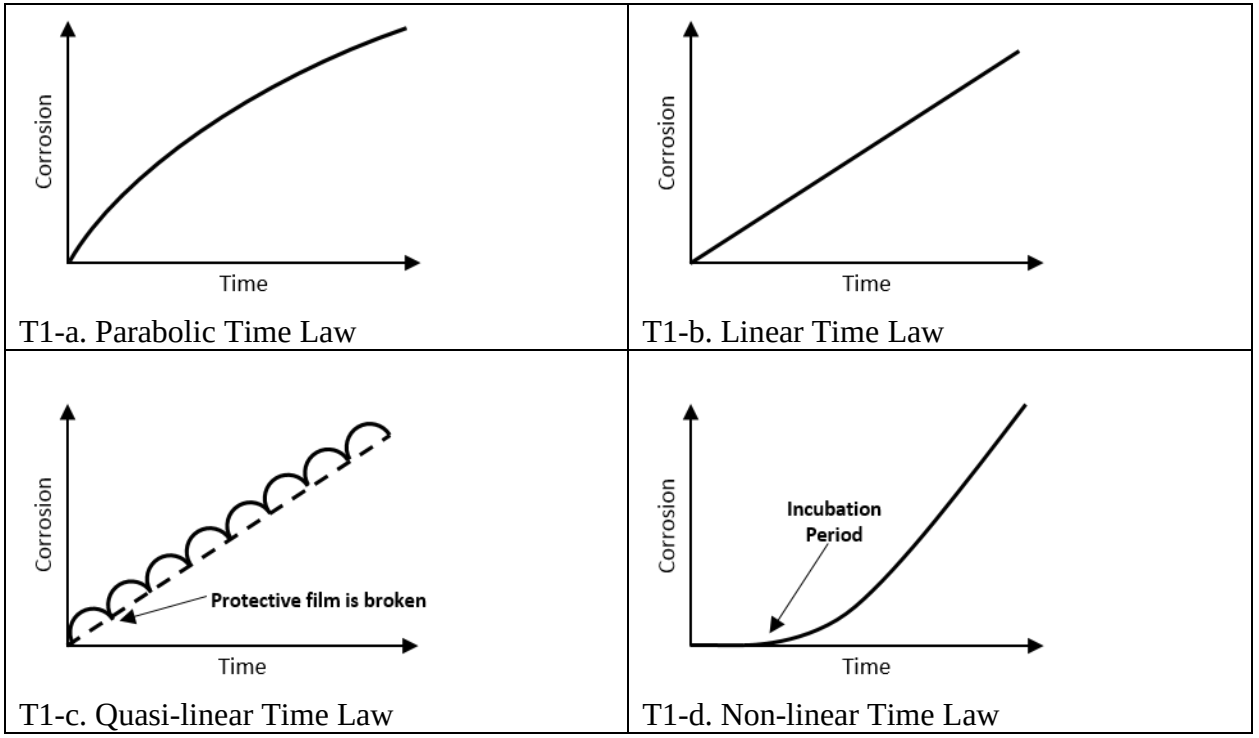
A comprehensive "general theory" that can explain the range of these issues encountered in practice is not currently available (Burson-Thomas and Wood, 2017). There is also dearth of experimental data to aid our understanding of the interplay between the many variables contributing to flow-induced failures. It is, however, generally accepted that erosion corrosion may occur partly by mechanical processes (i.e. pure erosion or high shear stress) and partly by electrochemical (or chemical or dissolution or mass transfer) processes (Vassilou 2001). Syrett

believed in a version of erosion corrosion governed purely by electrochemical reactions (1976), while Matsumura posited, "countermeasures against erosion corrosion lie not in the field of electrochemistry but in […] fluid dynamics" (2012). It is not always possible to neatly isolate these phenomena in laboratory studies because attempting to recreate one process (e.g., erosion via particle impingement) will automatically allow for the other kind (i.e., electrochemical interactions depending on water chemistry) to occur between exposed metal surface of pipe and flowing water. Roberge (2004) draws on Chexal et al. (1998) to summarize damage mechanisms of both mechanical and dissolution types as shown in Table 1-1, where the damage dependency on both mechanisms is theoretically distinguishable. For example, the corrosion rates become increasingly dependent on mechanical factors (e.g., due to increase in flow rate) as one advances downward in the Table. The accompanying figures (T1-a through T1-d) are hypothetical depictions of mass loss rates that complement the descriptive "stages":

- ***Figure T1-a*** is the initial corrosion rate resulting from two opposing reactions: i) passivation by (primarily) oxide-layer formation over pipe walls and ii) corrosion of fresh copper as it interacts with stagnant water. Over time, a thick and stable oxide layer forms on the copper surface, the release of copper ions into water decrease, and the corrosion rate plateaus.
- ***Figure T1-b*** describes the condition where passivation and copper release rates due to pipe interactions with flowing water, its constituents and associated hydrodynamics are at steady state leading to a constant mass loss rate.
- ***Figure T1-c*** illustrates hydrodynamic removal of the protective layer that can still repassivate, and the damage rate over time looks similar to ***Figure T1-b***. ***Figures T1-b*** and ***T1-c*** can be considered tangents to the curve in ***Figure T1-a***, mathematically representing slopes.
- Finally, ***Figure T1-d*** elucidates what happens when mechanical damage primarily leads to accelerated material loss. An incubation period, depending on water turbulence, length of exposure and properties of the target material (Campbell and Carter 1961-62), precedes rapid damage and this can sometimes be expressed as in terms of a "critical velocity."

Table 1-1. Summary of erosion corrosion damage mechanisms

← Mechanical damage increases	Dissolution dominant	← Dissolution increases
	The oxide film grows in static aqueous solutions according to oxide growth kinetics. Corrosion rate is a function of the bare metal dissolution rate and passivation rate. The corrosion kinetics follows a parabolic time law (Figure T1-a).	
	Flow thins to an equilibrium thickness that is a function of both the mass transfer rate and oxide growth kinetics. The erosion corrosion rate is a function of the mass transfer and the concentration driving force. The erosion corrosion kinetics follow a linear time law (Figure T1-b).	
	The film is locally removed by either surface shear stress or dissolution or particle impact, but it can be repassivated. The damage rate is a function of the bare metal dissolution rate, passivation rate and the frequency of oxide removal. The damage kinetics follow a quasi-linear time law (Figure T1-c).	
	The film is locally removed by dissolution or surface shear rate and the damage rate is equivalent to the bare metal dissolution rate. The damage kinetics follows a quasi-linear time law (Figure T1-c).	
	The film is locally removed and the underlying metallic surface is "mechanically damaged" which contributes to the overall loss rate, i.e. the damage rate is equal to the bare metal dissolution rate plus a possible synergistic effect due to mechanical damage. The damage rate follows a non-linear time law (Figure T1-d).	
	The oxide film is removed and mechanical damage (cavitation, droplet impingement, etc.) to the underlying metal is the dominant damage mechanism. The erosion kinetics follow a non-linear time law (Figure T1-d).	
	Mechanical damage dominant	



T1-a. Parabolic Time Law

T1-b. Linear Time Law

T1-c. Quasi-linear Time Law

T1-d. Non-linear Time Law

Hotter temperatures, water recirculation systems and growing concerns over *Legionella pneumophila*

Erosion corrosion seldom occurs in cold water systems and, when it does, it only occurs in systems with excessive water pressure, i.e. > ~ 80 psig (5.44 atm), or poor workmanship (Myers and Cohen 1998). Failures are witnessed predominantly in hot water systems. Scardina et al. (2008) compiled and assessed CDA's forensic analysis records of copper pinhole leak failures from 1975-2004 and found that 34% of failures in the "Hot water category" were attributed to Erosion Corrosion. Furthermore, this was believed to be an underestimate of the total number of failures actually occurring in practice because erosion corrosion is often easily diagnosed by eye, and full forensic evaluations that would cause entry to the database result in under-reporting. "Excessive heating of water" was also cited as a causal factor for an additional 23% of failures, which might also indicate erosion corrosion failures which increase at higher temperature (Lane et al. 1971, Knutsson et al. 1972, Scardina et al. 2008). For comparison, erosion corrosion accounted for 24% of copper pipe failures reported in Japan in 1993 (Sumitomo 1994).

Residential water heating infrastructure and especially hot water pipe systems, have now been associated with the growth and spread of the bacteria *Legionella pneumophila*. Inhaling water contaminated with *Legionella* from building water systems (e.g., breathing *Legionella*-containing aerosols in the shower or those released from cooling towers) can cause Legionnaire's Disease (LD), a severe type of pneumonia. LD is currently the leading agent of waterborne disease outbreaks in the US, causes 8,000-18,000 hospitalizations every year with 10+% cases being fatal and is reportedly on the rise (CDC 2011, CDC 2016). Because of increasing concerns over this health risk, there is an increased impetus to raise water temperature to 60° C to better control this pathogen (Tiefenbrunner et al. 1992, Pedro-Botet 2002, Lévesque 2004, NRC 2006, Bartram et al. 2007, Brazeau and Edwards 2013, ASHRAE 2015). The newly launched risk management directives for reducing *Legionella* growth under the ASHRAE/ANSI Legionellosis 188 Standard call for active and preventative steps to control temperature, disinfectant residual and pH in tandem with constant monitoring of water quality inside buildings (ASHRAE 2015, BEL 2016, CDC 2016). The corrective actions can include elevated chlorine dosing and/or raising water temperatures above 66°C (or even 71-77°C) followed by intensive flushing to scour biofilms harboring legionella, which do not always work (ASHRAE 2000, Bartram et al. 2007, WHO n.d.). Even without shock chlorination or thermal shock treatment followed by flushing at increased water pressures, conventional hot water recirculation practices can exacerbate corrosion damage (Lane et al. 1971, Knutsson 1972). It would be predicted that increased temperatures will sometimes markedly enhance the likelihood of erosion corrosion damage in systems that were immune to such problems near the 48° C temperature set-point recommended by US EPA (Gates 2012). Myers and Obrecht (1972) noted that "potable water should never be heated above about 60°C if corrosion is to be minimized" without providing data to support this assertion. Lane and colleagues, however, did find that at "high" velocities of 3-5.6 ft/s (or, 0.9-1.7 m/s), corrosion damage at 80°C was worse than that at 60°C (1971). In contrast, Kristiansen's exploration of copper corrosion w.r.t. temperature showed for conditions between 30°C-70°C, the worst corrosion rate was determined to be at 60°C. His testing specifically focused on the role of carbon dioxide and natural organic matter in water affecting corrosion rates and showed hotter temperatures alone do not always lead to severe corrosion (Kristiansen 1977).

Deficiencies in reviewed theories

After reviewing the literature and compiling possible fundamental explanations, it was apparent that even the classic description of such failures was deficient. For instance, accelerated localized corrosion driven by fluid velocity alone has never been proven to physically erode the underlying metal or protective scale. Syrett also underscores this (1976) by stating that mass transport to and from the metal surface usually determines the rate of corrosion and while velocity does influence mass transfer, it is not the sole factor. Additionally, some authors argue that erosion corrosion is caused by rapidly flowing liquid, gas bubbles, and suspended particles (Cohen and Lyman, 1972; Knutsson, et al., 1972; Myers and Obrecht, 1972) while others think it is also caused by a concentration cell phenomenon (Obrecht and Quill, 1960f).

Myers and Cohen (1998) investigated more than 100 incidents of erosion corrosion of copper tubes in the field (over 95% of which happened in circulating domestic hot water systems), and developed empirical equations that attempt to predict rates of copper erosion corrosion. These equations take into account water hardness, reaming condition, and temperature to calculate penetration rates, and a system with unreamed cut tube ends that circulates *soft water* at temperatures in excess of 60°C was deemed the worst-case scenario. Strangely, no information was provided regarding the derivation of the equations, why critical parameters like velocity and water chemistry were not included, and/or the accuracy in predicting penetration rates with actual copper pipe failures in the field.

None of the previous studies actually isolated specific mechanistic causes of *erosion corrosion* failures. For example, Knutsson et al. (1972) speculated that erosion corrosion is abetted by gas bubbles and solid particles entrained in flow, and yet short-term preliminary testing of these ideas in subsequent tests performed by Coyne (2009) could not verify these expectations. The overarching roles of temperature and velocity in copper pipe failures by erosion corrosion, however, have been repeatedly emphasized in recommendations available in the literature and associated standards (see Table 1-2). From the table, it is apparent that velocity recommendations to avoid erosion corrosion are inconsistent across the literature; however, it is acknowledged that in the presence of abrasive particulates, failures can occur at much lower velocities (Oliphant 2010, CDA 2016). Roberge notes that emphasizing a single velocity value as a marker for initiation of erosion corrosion can be misleading in predicting service life of pipe metal; change in pipe diameter while holding other variables constant, for instance, alters the thickness of the velocity boundary layer and shear stresses at the pipe wall thereby changing the maximum design velocity value for preventing erosion corrosion (2004).

Table 1-3 lists individual factors (except velocity and temperature) that can influence erosion corrosion in plumbing systems that have been found in the literature and current standards. In addition to the hydrodynamic flow characteristics, water chemistry, and other extraneous variables that govern field failures, the test methods employed to study and recreate erosion corrosion in the laboratory can also influence our understanding of the phenomenon. Reliability, reproducibility, rapidity in obtaining results and most accurate simulation of field conditions are critical to preferring one method over another. Moreover, the ease of measuring electrochemical readings and weight/thickness losses of test specimens also determine the effectiveness of

apparatuses. While results from these short term tests are often extrapolated to give a constant corrosion rate, care should be exercised while interpreting such results as localized erosion corrosion in actual systems is relatively complicated (Roberge 2004). Typical experimental techniques used for erosion corrosion testing (in potable water applications and beyond) are summarized in Table 1-4.

Given the diverse variables and distinct phenomena believed to cause erosion corrosion in copper water systems, it is clear that a more holistic approach is required in defining the erosion corrosion framework.

Table 1-2. Velocity-Temperature recommendations to prevent erosion corrosion in copper tubing (Modified from Gates 2012)

<table>
<tr><th>Factor</th><th>Recommendations for prevention of flow-induced failures</th><th>Elaborations and/or associated conditions, if any</th><th>Reference</th></tr>
<tr><td rowspan="15">Water velocity*</td><td>< 1.5 ft/s</td><td>For water in continuously circulating hot water tubing</td><td>AWWA 1996</td></tr>
<tr><td>< 3 ft/s</td><td></td><td>WHO 2006</td></tr>
<tr><td>< 4 ft/s</td><td>For Type K pipe; velocities much lower for Types L and M.</td><td>NACE 1980</td></tr>
<tr><td>≤ 4 ft/s</td><td>For domestic hot water temperatures (<57°C); equivalent to 8 gallons per minute flow in a 1-inch Type K Copper tubing</td><td>Singley et al. 1984 (US EPA)
Lane 1993</td></tr>
<tr><td rowspan="2">~4 – 5 ft/s</td><td>These velocities and associated turbulence especially at high temperatures (71 – 82°C)</td><td>Obrecht and Quill 1961</td></tr>
<tr><td>At temperatures ~ 49 – 54 °C</td><td>Myers and Cohen 1998</td></tr>
<tr><td>< 5 ft/s</td><td>For waters below 60°C
< 3 – 4 ft/s for waters above 60°C</td><td>CCBDA 1997</td></tr>
<tr><td>2 – 3 ft/s</td><td>For hot waters above 60°C</td><td rowspan="3">ASM 2005 (cited CDA)
PHCC NSPC 2006
CDA 2016</td></tr>
<tr><td>5 ft/s</td><td>Between 25°C – 60°C</td></tr>
<tr><td>5 – 8 ft/s</td><td>For cold waters (with positive scaling and pH ≥ 6.9)</td></tr>
<tr><td>< 1.6 ft/s</td><td>In heated water circulation systems</td><td rowspan="3">DIN EN 12502-2 2005</td></tr>
<tr><td>< 6.5 ft/s</td><td>For cold waters with longer draw-off periods (>15 minutes)</td></tr>
<tr><td>< 9.8 ft/s</td><td>For cold waters with intermittent service</td></tr>
<tr><td>2 ft/s</td><td>For hot water recirculation systems</td><td rowspan="2">PHCC NSPC 2006</td></tr>
<tr><td>4 ft/s</td><td>For cold waters (with no scaling and pH ≥ 6.9)</td></tr>
<tr><td colspan="2"><table>
<tr><th rowspan="2">Type of water installation</th><th rowspan="2">Accessibility</th><th colspan="4">Max. permissible flow rate (ft/s) at mean temperatures (°C)</th><th rowspan="2">Remarks</th></tr>
<tr><th>10°C</th><th>50°C</th><th>70°C</th><th>90°C</th></tr>
<tr><td>Distribution Main</td><td>Exchangeable</td><td>13.1</td><td>9.8</td><td>8.2</td><td>6.6</td><td></td></tr>
</table></td><td>Mattsson 1980 (from SBPPB 1970)</td></tr>
</table>

		Not exchangeable	6.6	4.9	4.3	3.3	
	Pipe to water supply point	Exchangeable Not exchangeable	52.5 13.1	39.4 9.8	32.8 8.2	26.2 6.6	#
	Continuous flow/circulation		6.6	4.9	4.3	3.3	$
Temperature	< 60°C						Myers and Obrecht 1972 Myers and Cohen 1998
	Erosion corrosion worse at 80°C than at 60°C		At "high" water velocities of 3 – 5.6 ft/s				Lane et al. 1971

Exceptions to the low velocity recommendations (as pointed out by Nicholas and Gates 2012) are:
- *British Standard BS 6700 (1987 Edition):* which allows 6.5 – 8 ft/s for waters above 60°C; this standard has been revised several times and is now superseded by BS EN 806-5:2012. The latter standard does not have provision for velocity constraints (not validated by authors of this paper).
- *Australian Standard AS 3500.4 (2005):* allowed ~ 10 ft/s for waters at any temperatures (since it did not differentiate between hot and cold waters). The flow velocity has been updated in the newer standard AS 3500.4 (2015) and capped at 4 ft/s for circulating copper pipes, while for other heated water it remains 10 ft/s.

Footnotes:
- Very high flow rates create a corrosion risk and are accepted in only this type of installation (pipe to water supply point)
$ - For dimensioning, use 1.0 – 2.6 ft/s

Table 1-3. Factors besides velocity and temperature contributing to erosion corrosion

Factor	Role in preventing or exacerbating flow-induced failures	Elaborations and/or associated conditions, if any	Reference
pH	"Low" pH is more conducive to erosion corrosion	Condensate containing carbon dioxide (i.e. "low" pH) can be harmful at "lower" threshold velocities compared to high pH water; treatment with caustic soda increases pH decreasing EC rates	Lane et al. 1971 Syrett 1976 Campbell 1982
Flow Duration	Intermittent flow reduces instances of erosion corrosion	Experiments with flow duration less than 25% of total time showed no signs of attack	Knutsson et. al. 1972
Particulates/ Suspended Solids	Erosion corrosion […] mitigated by ensuring that […] "abrasive suspended solids are not present in the water"	–	Myers and Cohen 1998
	Failures can occur much faster if particulates are present	Can happen at velocities much lower than 6 ft/s if abrasive particulates are present	Oliphant 2010 CDA 2016
	Presence of sand in seawater detrimental […] and may worsen erosion corrosion	Dependence on sand content, size of sand particles, flow profile, magnitude of impingement, and water chemistry	Schleich 2004
Air/Gas Bubbles	Presence increases likelihood of failure	In conjunction with high velocities and reduced static and/or dynamic pressure	Gilbert and LaQue 1954 NACE 1980 DIN EN 12502-2 2005
Dissolved Oxygen/ Dissolved Carbon Dioxide	Low oxygen content decrease possibility of erosion corrosion	High velocities would not cause erosion corrosion in deaerated waters even if it is moderately corrosive	Knutsson et al. 1972
	High concentrations of CO_2 and O_2 found in most "aggressive" waters	–	Obrecht and Quill (1960d)
	Deaerated water less corrosive	–	Obrecht and Quill (1960c)

	Deaeration of seawater substantially reduces erosion corrosion	–	Shifler 1999
	Erosion corrosion highly promoted when CO_2 > 10 ppm	With low hardness waters (non-scaling) and temperatures higher than 43°C	PHCC NSPC 2006
High turbulence	Sharp bends like in elbows, plug tees and poorly designed couplings are especially prone	Owing to high localized velocities	NACE 1980 Mattsson 1980 Mazumder 2004
Water Hardness	Increasing hardness reduces corrosion	Tests with sodium zeolite softened and blended hard waters at 60 and 110 ppm.	Obrecht and Quill (1960e)
	Soft water (that is not "stabilized") can corrode copper pipes and metal surfaces	Does not form protective film on pipe walls	NACE 1980
	Excessively hard water can have corrosion tendencies	No specific threshold hardness values defined	NACE 1980 WHO 2011
Water pressure	High pressures increase likelihood	Pressures greater than 80 psig or 5.4 atm	Myers and Cohen 1998
Impingement angle	Worst impact at 20 degrees	–	Schmitt Jr. 1979
Corrosion inhibitors	Treatment with silicates can sometimes promote a protective deposit reducing EC		Lane et al. 1971
Natural Organic Matter (NOM)	Worsens erosion corrosion	When NOM is present alongside Carbon Dioxide and at increased temperatures	Kristiansen 1977
Manganese Content	Worse in conjunction with soft waters	Referred to as "soft water pitting" and usually restricted to the hottest parts of hot water systems	Campbell 1954
Chlorine Content	Free chlorine, chiefly responsible for copper corrosion and effect is accelerated at lower pHs (< 7 pH); no specific reference to erosion corrosion		Atlas et al. 1982
Pipe diameter	*Larger pipe diameter increases* erosion corrosion rates by increased turbulence	Experiments conducted over a year showed large diameter pipes exhibited erosion corrosion as opposed to smaller ones at similar	Knutsson et al. 1972

		velocities possibly because of higher turbulence due to bigger Reynolds numbers	
	Smaller pipe diameter increases erosion corrosion rates by reducing "breakdown velocity"	Shear stress on the passive film on pipe wall increases leading to its breaking down/metal removal as pipe diameter decreases thereby increasing corrosion mass transfer from/to the pipe surface; "breakdown velocity" at which failures occur, thus, reduced	Schleich 2004
Surface Roughness	Smoother the pipe surface, lesser the likelihood	Increase in surface roughness is usually a consequence of erosion corrosion, which in turn exacerbates damage rate. A near-linear dependence between mass transfer indicated by the Sherwood number (Sh = ratio of total mass transport to that by molecular diffusion) and turbulent flow pattern or Reynolds number (Re = ratio of inertia force to friction force) as a consequence of increased surface roughness demonstrated by the equation $Sh = 0.01 \cdot Re \cdot Sc^{0.33}$ (Sc=Schmidt number)	Chexal et al. 1998 Poulson 1999 Roberge 2004
Sizing in pipe systems	Oversized circulation pumps and/or undersized distribution lines are "a recipe for disaster"		Villalobos 2007
Workmanship	Flared joints worse	At high velocities, erosion corrosion more easily possible than with capillary fittings	Knutsson et al. 1972
	Design faults, incorrect installation or poor workmanship increase likelihood of attack/failure	Includes unreamed cut tube bends, globules of solder on the inside surface in the joint area, tube ends not fully inserted into fitting prior to soldering, tube ends not cut square, dents/dings in tube, and tube crimped during bending.	Cohen 1993 Myers and Cohen 1998 DIN EN 12502-2 2005
	Reduced pipe efficiency due to increased friction loss; protrusions due to improper adjustments between pipe ends and outlets leading to increased turbulence		Schleich 2004

Table 1-4. Experimental techniques used to study erosion corrosion in various fluid conditions (compiled partly from Syrett 1976, Roberge 2004)

Test method	Description
a. Simulated Service Test/Flow Systems	Involves tests which reproduce field conditions to the extent possible. Forcing liquids to flow through pipe specimens to simulate service failures seen in domestic water systems is one example (Knutsson et al., 1972). There is a clear emphasis on pipe design and layout, flow rates, and water chemistry similar to what is typical in service.
b. Rotating Spindle and Disc Tests	Cheap and convenient, the rotating spindle tests involve a metal disc specimen axially mounted on a spindle being rotated about its axis in a tank filled with liquid being studied. Since the linear velocity of the disc increases from zero (at its center) to a maximum at the periphery, effects of velocity on corrosion rate can be calculated. Rotating disc tests are carried out by attaching flat plate specimens to the outer edge of a non-conducting, corrosion resistant disc and rotated in a manner similar to the spindle tests. The fluid flow characteristics in these tests rarely resemble those in the field; the results should, thus, be "interpreted with caution".
c. Rotating Cylinder or Drum Test	Cylindrical specimens are axially mounted on a spindle which is then rotated in a tank with test liquid. The flat ends of cylinders are insulated, the curved surfaces are exposed to the liquid and all points on its surface are at a constant velocity. This velocity can be changed by adjusting the rotation speed.
d. Multi-velocity Jet Test	Test coupon specimens are positioned in a pipe parallel to the flow direction and upstream from a nozzle fitted with appropriate orifice plates. The liquid velocity striking a test coupon depends on the orifice diameter. Liquid velocities can be easily varied thereby allowing multiple tests to be setup in parallel and the results compared.
e. Jet Impingement or Submerged Impinging Test	Involves a liquid jet impinging from a nozzle on a test specimen (say, a flat copper plate) immersed and held stationary in the same liquid (Poulson 1983, Neville and Wang 2009). A variation of this test is a free jet as opposed to the submerged one previously described. Owing to the perpendicular nature of the flow w.r.t. to the specimen surface, the critical jet velocity for erosion corrosion would be much lower than the breakaway velocities determined from other tests.
f. Jet in Slit Test	This technique developed by Matsumura involves a test liquid (usually, 1–3% $CuCl_2$

	solution as Cu^{2+} ions accelerate corrosion in copper alloys) at low pH injected through a narrow gap causing local depressurization and then impinging from a nozzle at a right angle eventually flowing in a radial direction over a round metal specimen (2012).
g. Brownsdon and Bannister Test	This test is used to estimate minimum seawater velocity required to cause erosion corrosion. Test specimens are fully immersed in natural seawater at 60°C subject to a 0.4 mm diameter submerged jet positioned at a 1-2 mm distance and air is forced through at high velocity for two weeks (UK MOD 1969).
h. Efird's Test (used first used by Efird 1977)	Test specimens (flat plates) are placed in tube shaped resin holders and positioned along the flow path of a circulating loop, i.e. water flows parallel to the test specimen and different waters like seawater (Efird 1977) and 3% NaCl solution (Sekine et al. 1991) can be tested.
i. Synergism between Wear and Corrosion Test	This test is actually a standard which offers a choice of many wear tests involving corrosion (***Erosion-only Studies*** below lists a few examples) to calculate material losses occurring as a result of interactions between erosion and corrosion in that system (ASTM 2009). A multitude of wear tests undermines the accuracy of the calculated material loss rate because the latter depends on the test chosen. The standard can also not be used for materials where corrosion products like oxides form on the surface causing weight gain.
EROSION-ONLY STUDIES	
j. Cavitation Erosion Test using Vibratory apparatus	Test specimens are immersed in the liquid and a vibratory apparatus (like, an ultrasonic processor) is used to produce cavitation damage on them. The test "induces formation and collapse of cavities in the liquid, and the collapsing cavities produce the damage and erosion (material loss) of the specimen." (ASTM 2010a)
k. Liquid Impingement Erosion Test	Also called the "rotating arm method," specimens are rotated at high rotational velocities through suspended drops to see the effect. This method, however, is mostly restricted to studying erosion in aircraft leading edges and helicopter rotor blades. (ASTM 2010b)
l. Solid Particle Impingement Test	Gas-entrained solid particle impingement on metal specimens via nozzle jet type erosion equipment. Primarily used as a screening test for ranking erosion characteristics of different materials for the same solids type (ASTM 2013a), but not used for evaluating effectiveness in potable water applications.

REVIEW OF MECHANISMS CONTRIBUTING TO EROSION CORROSION

A number of mechanisms are likely involved in a range of failures observed in practice and that collectively fall under a broad category of '*flow induced* failures.' In and after the fact evaluation of field failures, it is usually not possible to identify the precise conditions or causal mechanisms inducing the failure (Figure 1-4). Corrosion effects, whether uniform or localized, only can increase the degree of pipe damage and may even be the dominant mechanism of attack.

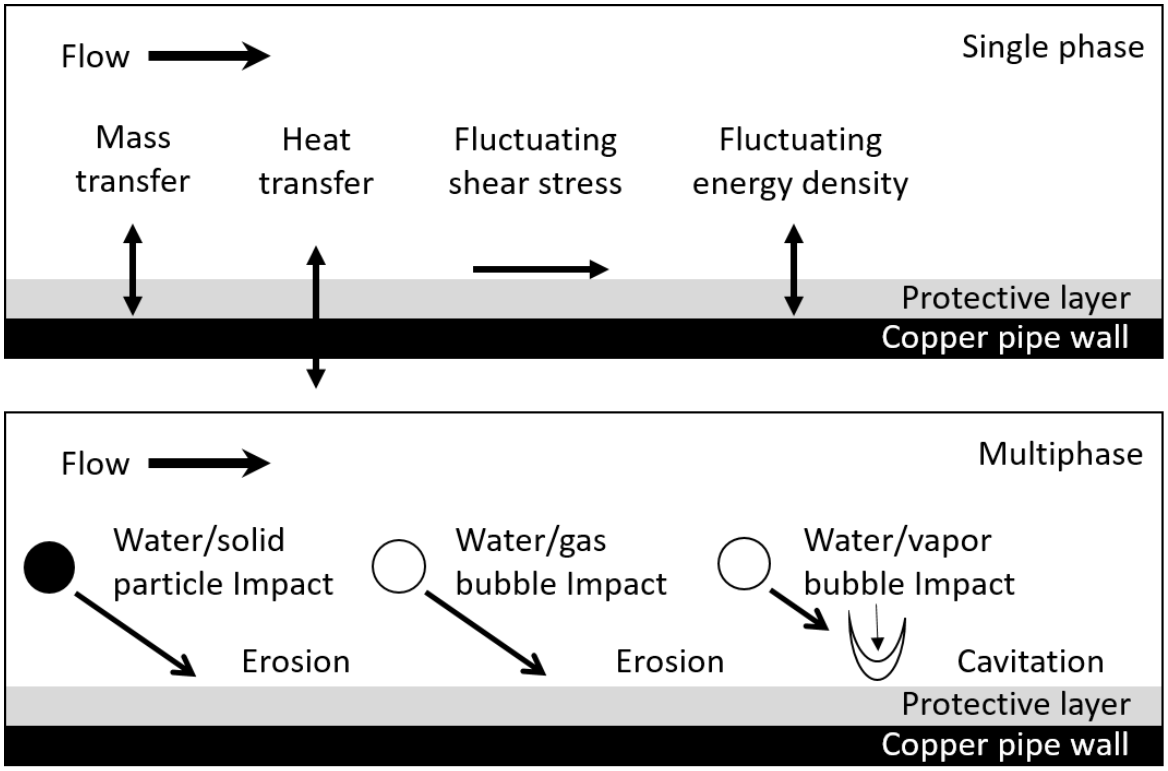


Figure 1-4. Fluid-wall interactions in flow systems
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Concentration Cell Corrosion

Concentration cells arise from electrochemical differences on different sections of copper pipe surfaces. For example, a different level of oxygen at two points of a copper pipe surface (Wood and Fry 1990) creates a voltage in which the high oxygen area becomes the cathode and the low oxygen area becomes the anode (Obrecht and Quill 1960f, Bengough and May 1924). A similar condition would occur when differential flow patterns create differences in oxygen or disinfectant levels on different sections of pipe. (Evans 1937, Novak 2005). Differential flow can also develop on surfaces at the microscale. For example, if a deposit or burr is present on the inner wall of a copper pipe, the resulting obstruction to flow can create extreme local turbulence and possibly

reach velocities up to 50X the bulk water velocity (Landrum 1990) immediately downstream of the obstruction that could enhance delivery of oxygen.

Dependent on water chemistry and the type of metal, pipe surfaces exposed to a high flow rate could become highly anodic or cathodic relative to areas of the pipe surface exposed to a low flow rate or stagnant conditions. This section reviews the basic electrochemical theory related to this phenomenon, describes practical situations in which differential flow arises in plumbing networks and might contribute to erosion-corrosion type service failures.

Concentration Cells Formed by Differential Flow

A concentration cell can develops whenever different portions of a metallic pipe surface are exposed to differing chemical conditions (Obrecht and Quill 1960f). The resulting electrochemical imbalance can create an electrochemical potential, separation of anode and cathode, and induce electron flow through the metal. In classic pitting corrosion, electrons are produced at the anode (the active site of the corrosion) (Figure 1-5):

$$Cu^0 \rightarrow Cu^{1+} + e^- \qquad \text{(Anodic Reaction for Copper).}$$

These electrons pass through the pipe to the cathode where they are consumed by reactions usually involving common potable water oxidants like dissolved oxygen or disinfectants:

$$0.25\ O_2 + e^- + H^+ \rightarrow 0.5\ H_2O \quad \text{(Cathodic Reaction with Oxygen).}$$

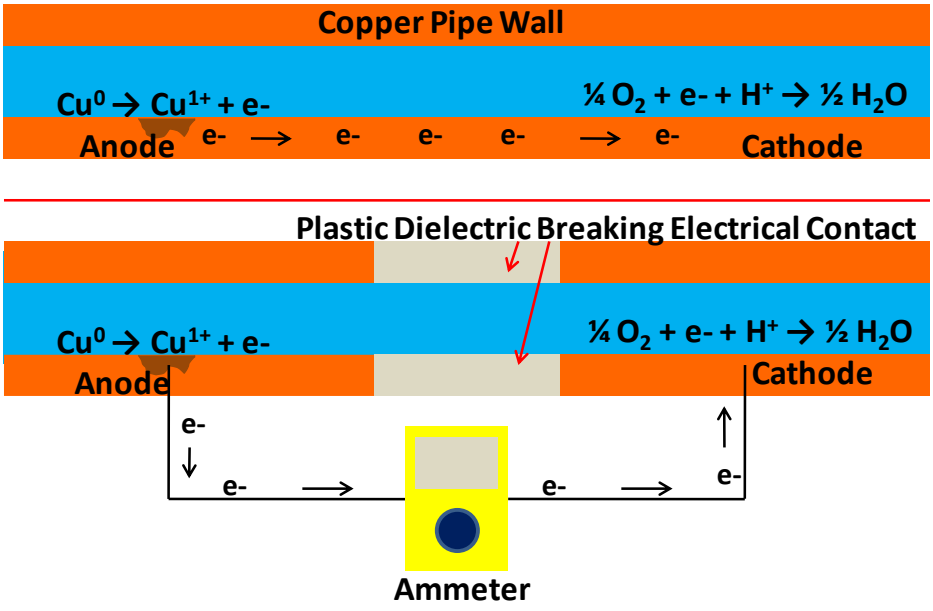

Figure 1-5. Key Reactions on Anodic and Cathodic Regions of the Pipe Surface Produce Electron Flow through the Metal (Above). If the Anodic and Cathodic Regions are not in Electrical Contact, the Resulting Voltage and Current could be monitored with a Simple Multimeter (Below).

Differential aeration cells are formed when the oxygen is more readily available on one portion of a metal surface than another (see Figure 1-6 for an iron differential cell illustration). The portion of the metal exposed to higher oxygen becomes electron deficient due to faster rate of reduction, and electrons flow through the metal from low concentration towards higher concentration. Thus, the area of the metal exposed to higher oxygen becomes the cathode, consuming electrons flowing from the anode. This has been well documented for corrosion occurring in a drop of water on an iron metal surface. The overall corrosion reaction for iron can be written (Equation 1-2).

$$4Fe + 3O_2 + 2H_2O = 2Fe_2O_3.H_2O \quad \text{(Equation 1-2)}$$

Iron/Steel + Oxygen + Water = Rust

The cathodic reaction predominantly occurs in the oxygen rich outer edge of the drop, and the anodic reaction occurs at the center. Electrons are transported through the metal, and as a result the metal at the center of the drop is rapidly eaten away.

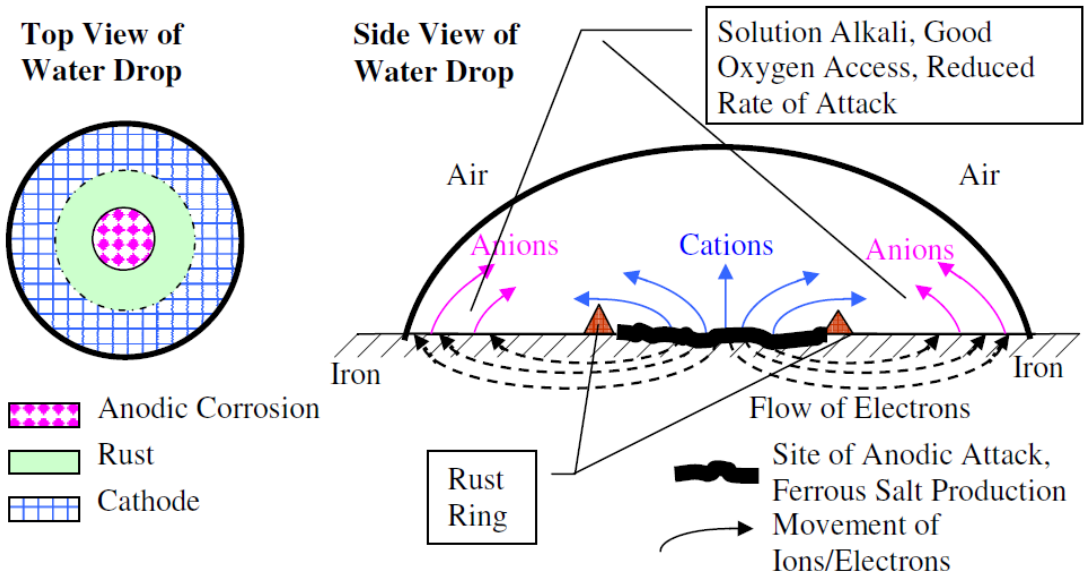

Figure 1-6. Corrosion within a drop of water on iron (after Evans, 1937)

Considering the analogous situation for an iron pipe in service, it is predicted that the metal will be eaten away more rapidly on the iron pipe surface exposed to less turbulent water flow, since oxygen concentrations will be lower at this surface. Witter et al. (2000) have demonstrated a flow dependency on corrosion of red water which might be related to this behavior.

Strong concentration cells can also form on copper tube used in domestic water supply. If particulates settle or otherwise deposit on the pipe wall, the portion of the tube under the deposit is cut off from the main oxidant (e.g., oxygen, chlorine, or chloramine). This results in a large difference in oxidant concentration over the surface. The oxidant deficient area under the deposit can cause localized attack via a phenomenon termed

"pitting corrosion." Once established, relatively thick deposits form as the result of local corrosion, which can stabilize the concentration cell until the pipe wall under the deposit is eaten away and a leak forms.

However, for copper tube and other more noble metals, under flowing conditions oxygen is continually transported to the pipe surface, and less oxygen is consumed due to a low rate of corrosion relative to iron. Thus, there is a lesser difference in oxygen concentration over the surface. It is also predicted that for copper, the anodic reaction can become the rate limiting step, in that the overall corrosion rate is controlled by the concentration of cupric and cuprous ions near anode surface (Evans, 1937). In this event, the portion of the copper pipe surface exposed to higher flow would become the anode, as it has the lower concentration of cupric and cuprous ions. This is the exact opposite of what occurs when dissolved oxygen was the rate limiting step.

Copper corrosion rates are also very sensitive to the formation of scale (cupric rust), which forms a barrier to diffusion of oxygen and cuprous/cupric ions. If higher velocity water were to cause this scale to detach via erosion, portions of the pipe surface exposed to higher flow rates would tend to become the anode due to greatly reduced levels of cuprous/cupric ions near surfaces with less scale. This exacerbates the extent of corrosion occurring at points exposed to greater turbulence or highest velocities.

Corrosion reactions are quite complex, and the above tendencies can be expected to change as a function of temperature, pH and other chemical constituents in the water. It is nonetheless interesting that portions of iron metal exposed to low flow are eaten more quickly, whereas copper metal may be consumed more rapidly in areas of higher flow (Figure 1-7).

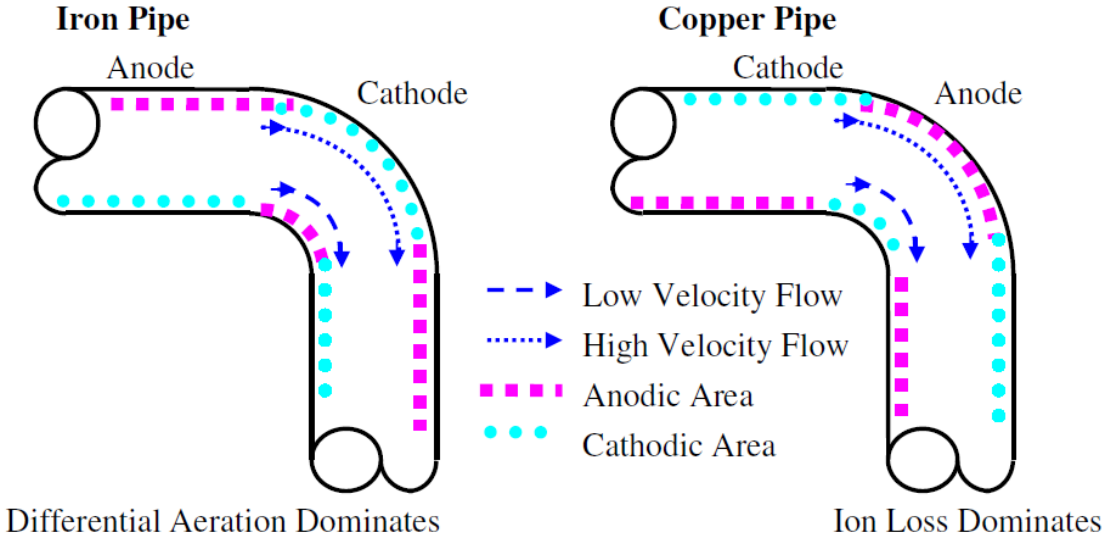

Figure 1-7. Hypothesized location of corrosion due to turbulence for iron and copper pipe

The electrochemical imbalance can also be created by differential flow as a result of enhanced transport near the surface of the pipe that is exposed to more turbulence. Specifically, the portion of the surface with higher flow will be exposed to higher concentrations of corrosion reactants (oxidants like O_2 and Cl_2) and lower concentrations of corrosion reaction products (metal cations like Cu^{2+} or Pb^{2+}) than the rest of the pipe (Figure 1-8). The net result of these imbalances depends on electrochemical kinetics in the specific system. Specifically, if the anodic reaction is rate limiting, the removal of the reaction product such as Cu^{+1} (Wood and Fry 1990) will have a disproportionate effect, and a local excess of electrons will be created at the surface subject to high flow (Figure 1-8). There will then be a net flow of electrons to the portion of the pipe surface exposed to lower flow where the cathodic reaction will occur (Figure 1-8).

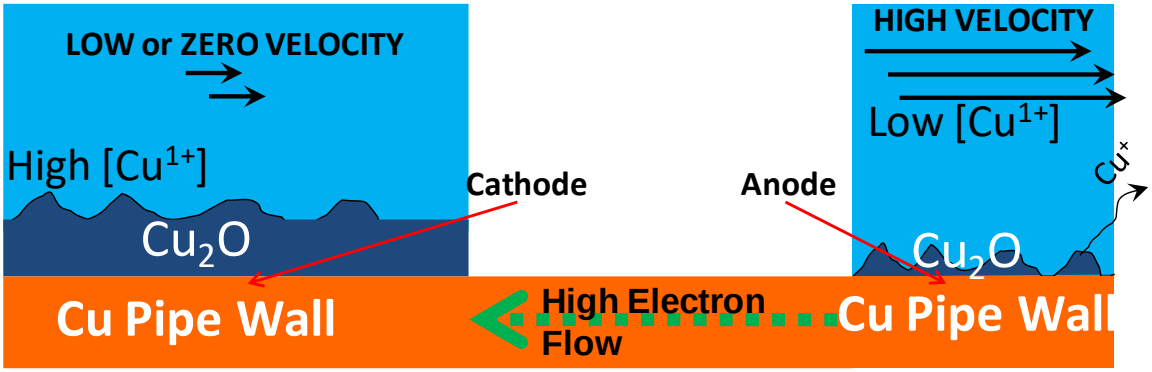

Figure 1-8. Simplified Schematic of Concentration Cell Pitting Corrosion for Anodically Limited Reaction (Nguyen and Edwards 2006)

If the cathodic reaction is rate limiting, the higher concentration of oxygen or disinfectant at the surface exposed to high flow, due to the enhanced diffusion of oxygen to the surface (Obrecht and Quill 1960f)) having a disproportionate impact (Figure 1-9). This would create a relative deficiency of electrons in the portion of the metal surface exposed to higher flow, and the anodic reaction would then occur at the portion of the pipe surface exposed to lower flow. In that case the direction of electron flow through the metal and the location of the anode and cathode would then be reversed from the situation described in Figure 1-8.

Differential Flow in Service

In a premise plumbing potable water system, concentration cells arising from differential flow could develop in a number of situations at either the macro or micro scale. For example, a home may have a section of copper plumbing leading to a kitchen faucet that is frequently used during the day at a typical maximum velocity of 8 ft/sec for washing dishes and preparing food. This branch of the plumbing system could be in electrical contact with other branches that lead to plumbing devices that are stagnant such as a second bathroom or an outside hose bib (Figure 1-10). These long periods of stagnation in seldom used plumbing fixtures can produce large areas of copper pipe surface that are exposed to relatively high concentrations of copper ions. Conversely, the frequent usage of the branch of plumbing leading to a kitchen would have relatively low concentrations

of copper corrosion products (i.e. Cu^{+1} and Cu^{+2}) and high levels of oxygen and chlorine in the water versus the less frequently used branch (i.e., copper ions are removed from the system while oxygen and chlorine are introduced to the premise plumbing from the main during periods of flow). Due to these differing chemical concentrations, entire sections of the plumbing network might therefore become anodic or cathodic to each another.

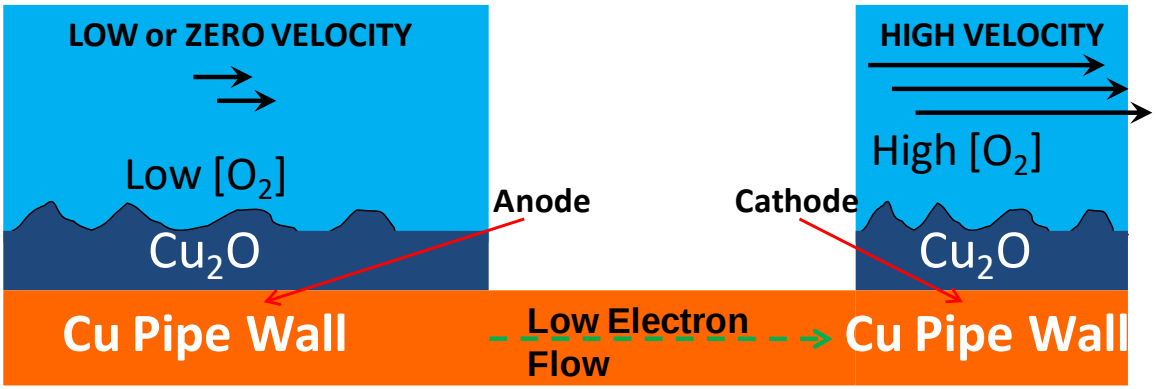

Figure 1-9. Simplified Schematic of Concentration Cell Pitting Corrosion for Cathodically Limited Reaction (Nguyen and Edwards 2006)

Differential flow can also develop on surfaces at the microscale (Figure 1-11). For example, if a deposit or burr is present on the inner wall of a copper pipe, there is an extreme local turbulence and high velocities up to 300 ft/sec (Landrum, 1990) immediately downstream of the obstruction (Figure 1-11). In this type of situation only a very small portion of the overall pipe surface will be exposed to the relatively high turbulent flow, a large portion of the pipe surface is exposed to relatively low flow, and a very small part of the surface (under the deposit) can be exposed to nearly stagnant conditions.

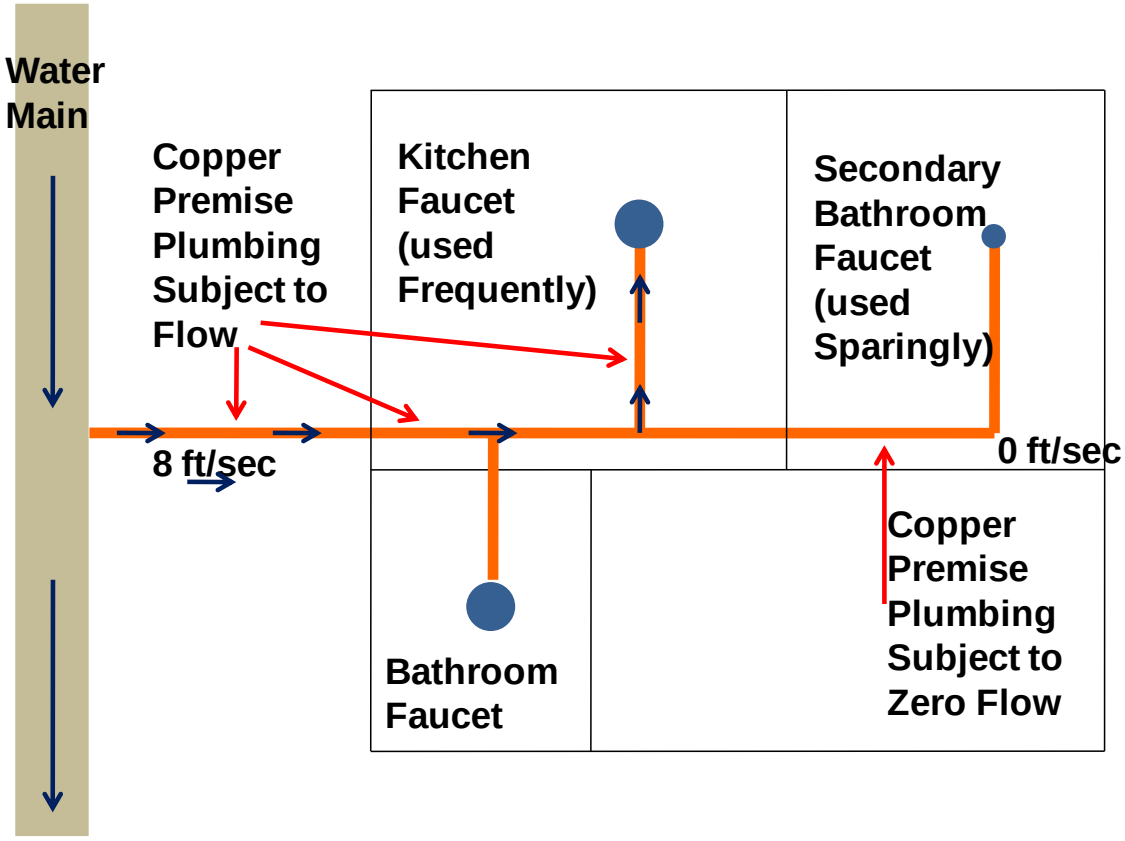

Figure 1-10. Conceptualization of Macroscopic Differential Flow Patterns that naturally arise from Different Water use Patterns in Separate Branches of a Premise Plumbing System

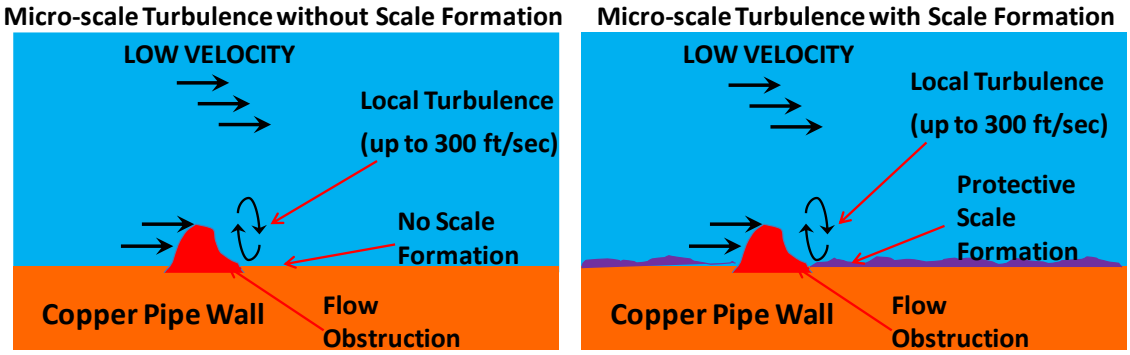

Figure 1-11. Schematic of Localized High Velocity and Turbulence which may form Downstream from an Obstruction (with and without Scale Formation)

Effect of Design, Installation, and Water Chemistry

The ultimate consequences of differential flow are determined by a number of factors. If numerous deposits are formed on the pipe surface or if joints are not deburred during installation, then microscale differential flow cells can occur with high frequency throughout the plumbing system. In other installation scenarios such situations may be rare or nonexistent. Maintaining maximum flows less than 8 ft/sec in cold water systems and 5 ft/sec in hot water systems, as per design recommendations of the Copper Development Association (2010), would also reduce the magnitude of differential flow concentration cells at either the micro or macro scale, when compared to situations that would arise if design velocities were 10, 20 or 30 ft/sec.

Water chemistry also plays a critical role because it controls the type of reactions and scale (i.e., copper rust layers) that form on the metal. As a relatively noble metal, corrosion of copper can be either anodically or cathodically limited depending on the water chemistry (Evans, 1937). As mentioned earlier, in some situations the portion of the surface exposed to the high flow will become anodic and in other situations the portion of surface exposed to high flow will be cathodic (Figures 1-8 and 1-9). But the water chemistry and the overall propensity for pipe failure due to differential flow can be influenced by the type and durability of scale that forms on the copper pipe surfaces at the anode or cathode, as formation of highly durable or protective scales at the anode could protect the surface exposed to flow and mitigate the strength of the concentration cell that is formed.

The chemistry of the water supplied and the mode of operation can also be influential. For example, if the water is operated in a continuous recirculation mode, the concentration of Cu^{+1} and Cu^{+2} reaction products may equilibrate in the bulk water and the concentration of dissolved oxygen and chlorine can become depleted. In such situations, the area of pipe exposed to high flow might not form a strong concentration cell relative to the situation that occurs in fresh water that has not previously contacted the copper surface.

In the vast majority of plumbing installations, water chemistries, and water use patterns that are encountered in premise plumbing, non-uniform corrosion arising from differential flow is of little consequence. It is only in very unusual cases that problems are observed. On the basis of this analysis, rapid failures are expected to occur from this mechanism if non-durable scale forms on the anodic pipe surface, if the anodic reaction is rate limiting, and if a small area of the pipe surface is subject to very high velocities due to a failure to de-bur or from formation of deposits (Figure 1-11). If all these factors are met, attack at a very small anode is supported by a very large cathode (Figure 1-12), and the attack is perpetuated by a failure to form a protective scale on the part of the surface exposed to high flow (Table 1-5).

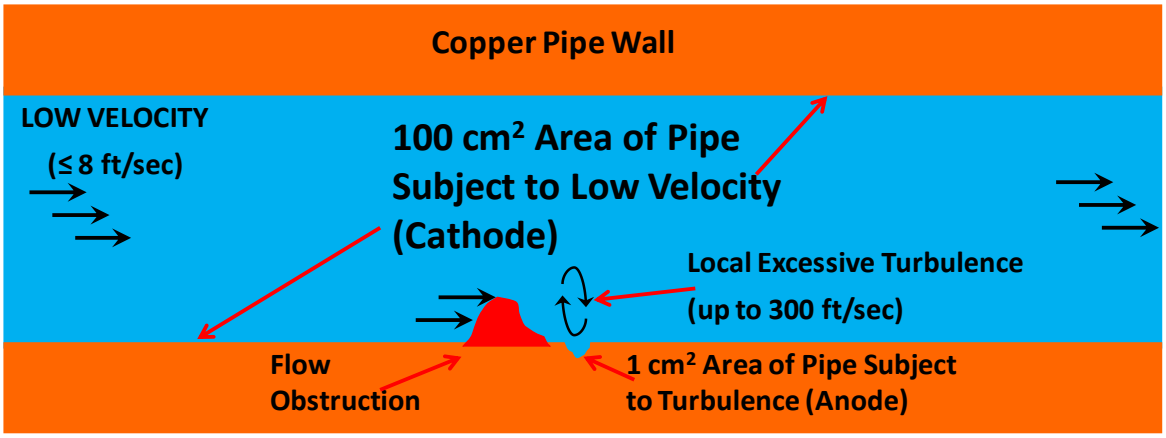

Figure 1-12. Simplified Schematic of Small Area (1 cm^2) of Pipe Subject to Turbulence and a Large Area (100 cm^2) of Pipe Subject to Low Velocity

Table 1-5. Simplified Example of Expected Failure Time among Concentration Cell Reactions Controlled Anodically and Cathodically for New ¾" Type M Copper Tube

Rate Limiting Reaction Controlling Concentration Cell	Measured Electron Flow (Current, uA)	Area of Anodic Portion of Pipe (cm^2)	Current Density (uA/cm^2)	Expected Time to Failure (Yrs)
Anodic Reaction	35	1	35	1
Cathodic Reaction	35	100	0.35	100

If the cathodic reaction is rate limiting, the very small area exposed to high flow becomes the cathode and the anodic attack is distributed over a much greater surface area (Table 1-6). It is therefore believed that water chemistry would control whether a pipe exposed to differential flow would last 100 years or fails in as little as 1 year (Figure 1-13).

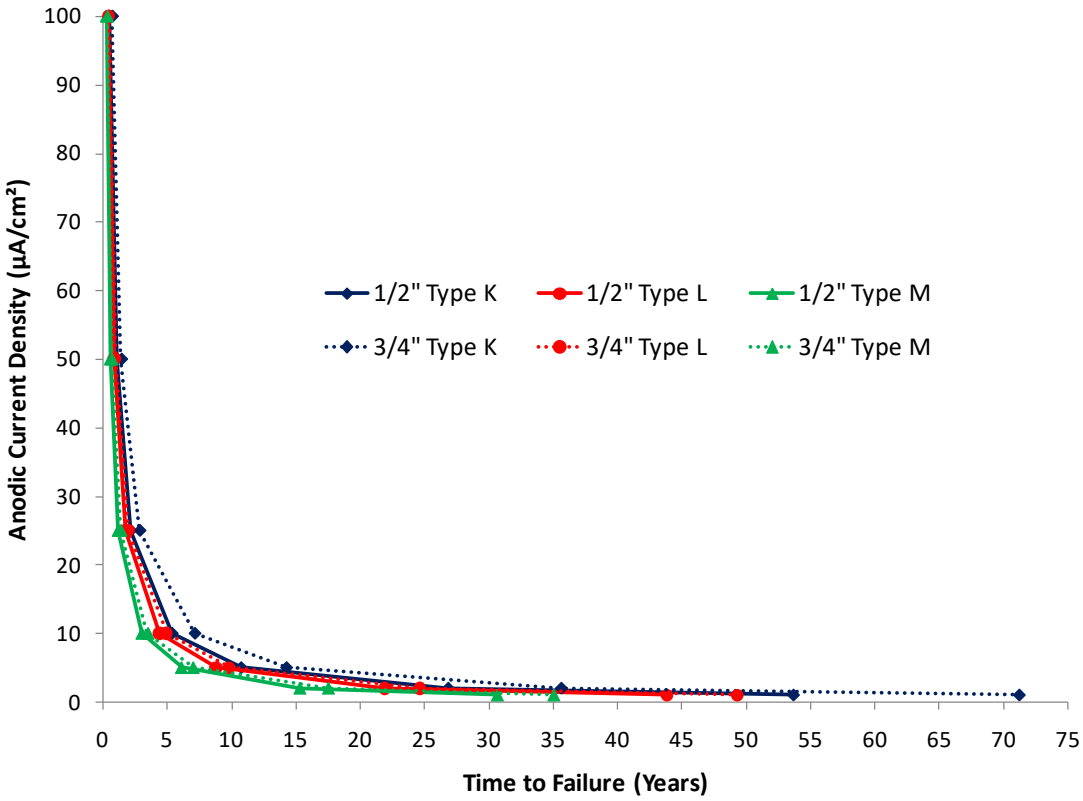

Figure 1-13. Anodic Current Density vs. Time to Failure for Different Types and Sizes of Copper Pipe

Unfortunately, at present, there is little to no research on the specific aspects of water chemistry that will determine scale durability, or whether copper corrosion will be subject to anodic or cathodic control. Indeed, there have been few systematic investigations into the veracity of the above hypothesis.

In seawater, the high values of the mass transfer coefficient at high velocities result in both an increase of the surface pH and of the dissolution rate of the film by diffusion of a soluble Cu (I) species. Localized attack in the erosive cavities gives rise to active–passive cells which are self-perpetuating due to the local hydrodynamic conditions established in them. (Bianchi et al. 1978, Bastidas et al. 2010).

Cavitation Bubble Implosion and Damage

Cavitation describes the spontaneous nucleation, growth and then collapse of gas or vapor bubbles when local hydraulic pressure drops below the gas saturation pressure or below the vapor pressure of water (Novak 2005). Liquids, therefore, are said to "cavitate" when pressure reduction causes formation and growth of bubbles (Brennen 2013). This can occur in systems where the flow velocity is very high and the direction of flow is sharply changed or it encounters flow obstacles like burrs, solder blobs and uneven corroded surfaces. Obstructions like valves or orifices downstream of a pipeline are especially prone to witnessing the "unwanted phenomena" of cavitation (Euler 1754,

Chan 2003, Wilson et al. 2006). In a plumbing fitting (like a 90 degree elbow), the centrifugal force flowing around a short bend radius at high velocity causes a pressure increase at the outer portion and a resultant lowering of pressure at the throat (CCBDA 1997).

Vaporous and Gaseous Cavitation

Classical cavitation experiments that disregard dissolved gas are not directly relevant to natural water systems and require a redefined cavitation inception number which considers dissolved gases. Vaporous cavitation occurs when the bubble is comprised entirely of water vapor, due to local solution pressure dropping below the vapor pressure and "boiling" the water at ambient temperature. The cavitation inception number is defined as

$$\sigma_{ci} = \frac{P_{fl} - P_v}{0.5\ \rho U^2} \quad \text{(Equation 1-3)}$$

where σ_{ci} is the cavitation inception number, P_{fl} is the fluid pressure, P_v is the vapor pressure of the liquid at a given temperature, ρ is the fluid density and U is the free stream velocity. The cavitation inception number σ_{ci}, is a dimensionless number used to evaluate the potential for cavitation in a system. Typically cavitation becomes a significant problem when σ_{ci} drops below 3, although the number has been known to vary depending on circumstances and the system. It has been noted that cavitation inception increases with higher dissolved gas contents (Brennen 1993).

Gaseous cavitation refers to bubbles comprised of dissolved gases and formed by a pressure drop below the saturation pressure of the constituent gases ($p_{fl} < p_g$). The distribution of gases in a water in equilibrium with the air are governed by Henry's Law

$$p_{gas} = kC \quad \text{(Equation 1-4)}$$

at a constant temperature, where p_{gas} is the partial pressure of the individual gas, k is Henry's constant and C is the concentration of the gas in air.

Typical vapor pressures of water from 10-40° C range from 0.012 to 0.073 atmospheres, whereas the total dissolved gas pressure of natural water is typically in the range from 0.8 to 1.2 atmospheres (Scardina et al. 2004). Decreasing the pressure to below the total dissolved gas pressure will tend to create gas bubbles at nucleation sites, as in the case of opening a pressurized carbonated beverage. The bubbles will begin to re-dissolve into the water if the ambient water pressure is increased to above the total dissolved gas pressure. The formation of gaseous cavitation bubbles is slower than vaporous, since the dissolved gases are present in the water at the ppm level and the bubble grows by diffusion, whereas vaporous water can form much more rapidly since water itself is the solvent.

Preliminary attempts to describe the effects of gaseous cavitation led to incorporation of total dissolved gas (TDG) into the classical cavitation inception formula (Naylor and Milliward 1984).

$$\sigma_{ci} = \frac{P_{fl} - (P_v + P_g)}{0.5\,\rho U^2} \quad \text{(Equation 1-5)}$$

where P_g is the total dissolved gas pressure. The main implication of the above equation is that gaseous cavitation occurs far more readily in practical situations in pipelines than does vaporous cavitation (Figure 1-14), which is to be expected considering that ambient pressure only needs to drop below about 1 atmosphere (total dissolved gas pressure) for gaseous cavitation to be possible versus below about 0.073 atmosphere necessary for vaporous cavitation.

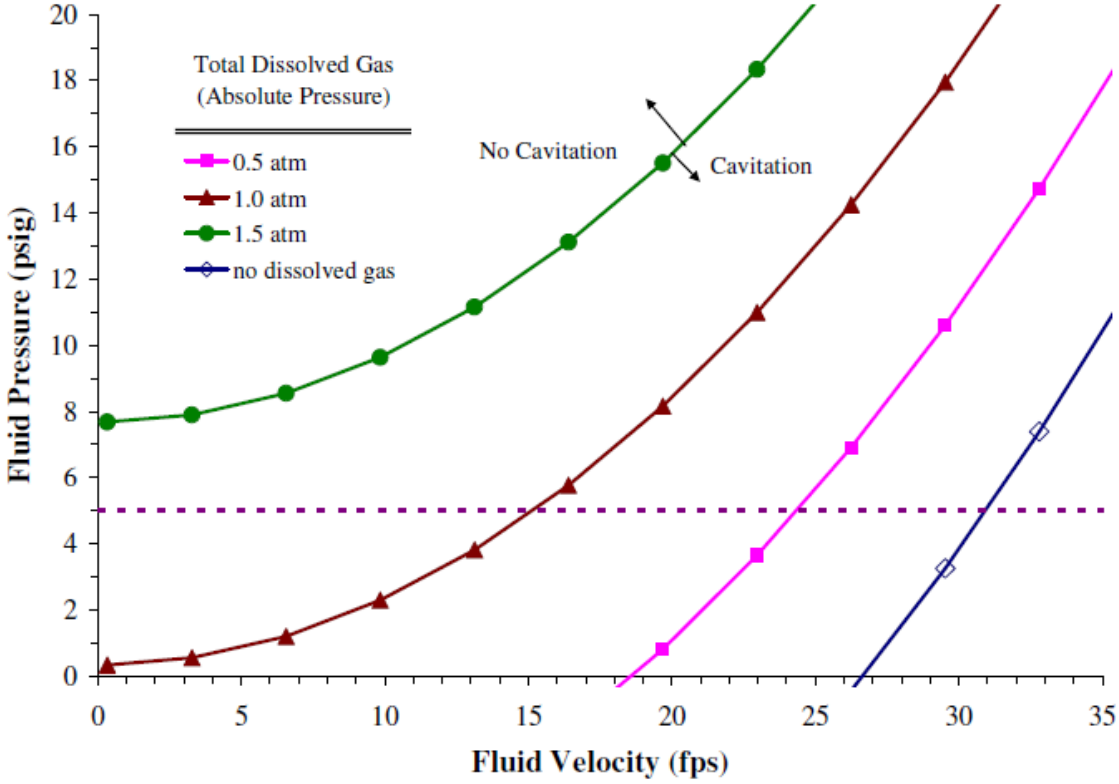

Figure 1-14. Comparison of Super- and Under-saturated Cavitation Inception to Pure Vaporous Cavitation (σ_{ci} = 3). Without dissolved gas in water, velocities greater than 30 fps are required for vaporous cavitation even at 5 pound per square inch gage (psig). However, if 1.5 atmospheres dissolved gas are present, gaseous cavitation will occur even without flow at 7.7 psig or less (Novak 2005).

Table 1-6 offers a comparison between vaporous and gaseous cavitation. As long as the water contains dissolved gas, as most potable waters will, gaseous cavitation will always occur much higher pressure and lower velocities than vaporous cavitation. However, given the kinetic limitations to gas diffusion into growing bubbles, it might be that

vaporous cavitation bubbles dominate in some circumstances. Bubble collapse and implosion pressures are often modified by the presence of other gases; if gas quantity is great, the slow nucleation of the cavity will produce less violent implosions (Koivula 2000). In theory, all cavitation occurring in natural waters will be either gaseous cavitation, or a combination of gaseous and vaporous cavitation. This is interesting, because the presence and specific role of dissolved gases are often ignored in prior research on the subject.

Table 1-6. Comparison of classical Vaporous and Gaseous Cavitation

Parameter	Vaporous Cavitation	Gaseous Cavitation
Bubble formation rate	Very quick on the order of thousandths of a second	Bubbles grow more slowly due to diffusion from bulk solution
Bubble disappearance	Vapor will condense in milliseconds once higher pressures are encountered	Bubbles disappear by dissolution of gases into the water (several seconds)
Implosion pressures	extremely violent	presence of dissolved gases smoothens pressure spikes (Lai et al., 2000)
Typical gas content	Almost entirely water vapor	Nitrogen, Oxygen, CO2, Cl2, Ar

Bubbles and Corrosion

Bubbles are believed to enhance corrosion via gas bubble impingement, bubble implosion from vaporous cavitation, and trapped gas.

Bubble Impingement

For either iron or copper, direct contact of bubbles on a pipe wall can result in loss of pipe material or, more importantly, deterioration of protective films that have developed on the pipe. Entrained gases are known to increase corrosion rates and decrease the velocity at which cavitation occurs (Obrecht et al 1960, Lagos 2001). Bubbles traveling in a continuous cloud could have a scouring effect on the metal and could damage it significantly by erosion even without implosion of the bubbles or air trapping. Air scouring – the deliberate injection of air to scour and clean distribution pipes, is a recognized practical application of this idea (Severn Trent Services, n.d.). The precise role of higher velocity, bubble size and concentration has not been evaluated experimentally.

Implosion

Bubbles consisting of water vapor are highly unstable and can collapse (or implode) when the bubble returns to a normal pressure region (Figure 1-15). The implosion creates "micro-jets" of water that can travel faster than the speed of sound and with pressures sufficient to physically gouge and damage metallic copper, often causing crater shaped material abrasions inside the system (During 1990, Siegenthaler 2000, Novak

2005, Merkle 2014). Plesset and Chapman (1970) estimated the velocity of the liquid jet, originating at the collapse of the bubble if attached on the solid wall, to be as high as 128 m/s. The micro-jets formed are extremely small and short-lived, but they are still very damaging; in some cases impacting metal surfaces with such force as to literally rip away minute amounts of metal (Siegenthaler 2000; Coyne 2009).

Bubble collapse after vaporous cavitation can occur with tremendous force and seriously damage metal due to creation of a shock wave (Figure 1-15). While pure vaporous cavitation probably does not occur in a water system saturated with dissolved gases, it is generally more damaging because of the forces involved and localized nature of the problem. Since dissolved gases cushion these implosions, damage from vaporous cavitation would be expected to decrease with higher gas content (Jang and Aral 2003), as opposed to the tendency that is actually observed in practice.

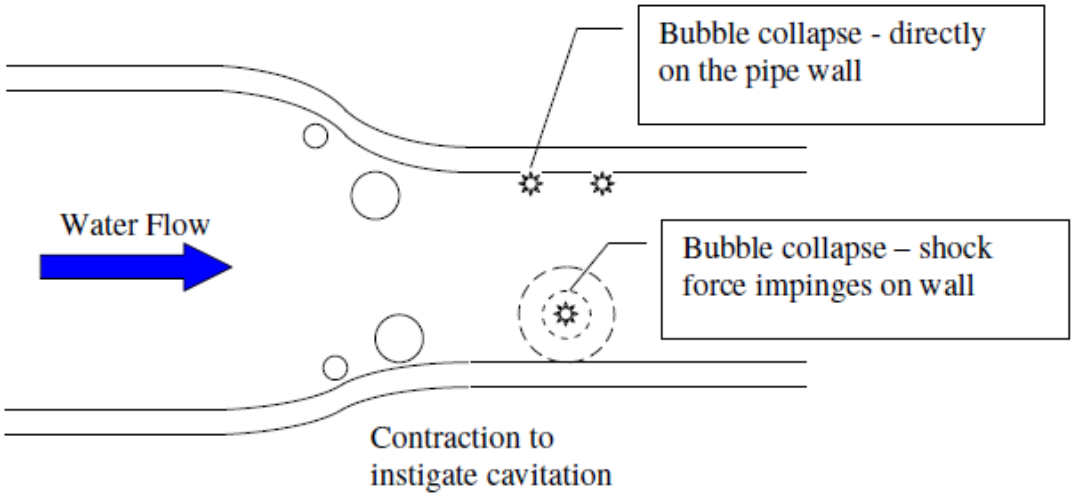

Figure 1-15. Bubble collapse/implosion (Novak 2005)

When the local pressure is higher than the total dissolved gas pressure, the bubble will disappear, sometimes violently. The maximum pressure from the bubble collapse is estimated at tens of thousands of pounds per square inch (psi) and the timespan of collapse can be less than a millisecond (Konno et al. 2001). Although theoretically this collapse occurs instantaneously after the bubble moves into an area of higher pressure, the bubbles can persist 20 times beyond the nozzle diameter in jet cavitation in tap water nearly saturated with dissolved gas even at pressures up to 72 psig (5.06 atm) (Nakano et al. 2001).

Trapped Gas

Bubbles that have formed may not travel along with the water flow but instead cling to the metallic surface of pipe (Evans 1937). In this case, corrosion would occur just outside of the air bubble (Figure 1-16). A bubble of air at atmospheric pressure would not be of much concern, as the oxygen in the gas would be gradually removed (Evans 1937), and the local concentration of dissolved oxygen would have started at only 8.4 mg/L at 25° C.

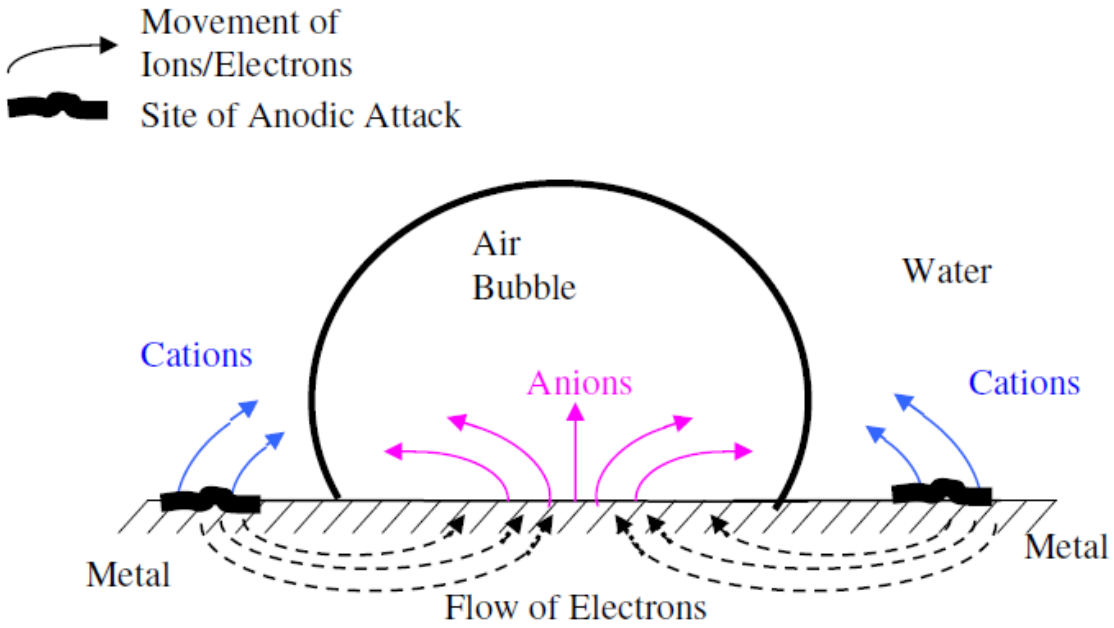

Figure 1-16. Corrosion of Metal in Presence of an Air Bubble (Novak 2005)

However, a bubble in a distribution system is not in a solution at atmospheric conditions, as even 20 psi gauge pressure is 2.4 atmospheres absolute pressure. In high-pressure lines such as those for high rise buildings or fire sprinkler systems, pressures can even exceed 175 psi (12 atm). This translates to 12 times the partial pressure of O_2 in trapped gas, and dissolved oxygen concentrations in the water immediately next to the bubble would approach 120 mg/l at saturation (e.g., 12 times the dissolved oxygen in equilibrium with gas at 1 atmosphere). This could drive massive concentration cells, since the water oxygen concentration would remain at or slightly below saturation.

If a pipe is partly filled with pressurized air, the oxygen present can also serve as a reservoir (Figure 1-17). In a copper pipe in service, it often takes only about 2 weeks of corrosion to remove all dissolved oxygen from water. But the oxygen stored in an air gap of .8-inches within a 1-inch pipe could fuel the equivalent of 4 years of copper tube corrosion, even without replacing the water (Figure 1-17). This trapped oxygen can therefore serve as a massive reservoir for aerobic reactions in the pipe, including corrosion or bacterial growth.

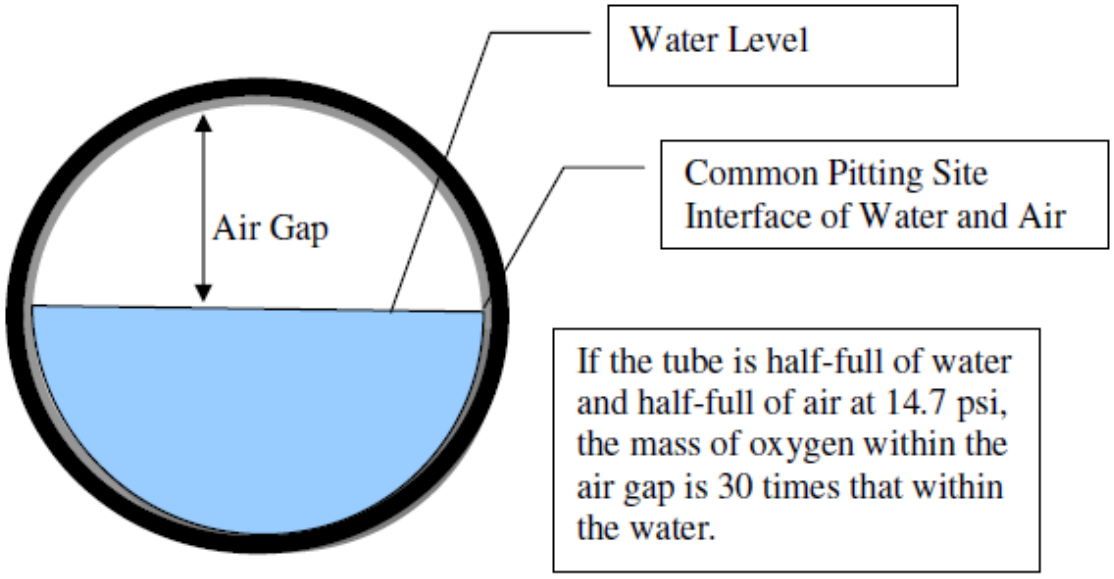

Figure 1-17. Trapped gas in a water pipe (Novak 2005)

Gaseous Versus Vaporous Cavitation

Gaseous cavitation was observed in the experiments performed by Novak (2005) even though theoretical calculations (using equations by Naylor and Millward (1984)) indicated that for the saturations and velocities being tested it should not occur. Novak (2005) speculated the possibilities that gaseous cavitation was occurring at the pump itself or that gaseous cavitation in distribution pipes occurs at higher inception numbers than commonly thought. In any case, because recirculating pumps are used in home and building plumbing, the implication is that cavitation may be widespread. Gaseous cavitation was also influenced by changes in temperature, initial dissolved gas concentration and water chemistry, pH in particular (Novak 2005).

Trends in pipe failures from erosion corrosion and cavitation are consistent with predictions based on gaseous, rather than vaporous, cavitation (Novak 2005). It is possible that the dissolved gases present in the tap water increase the persistence of the bubbles. Chan and colleagues suggested that cavitation played a significant role in valve damage in Hong Kong water lines and that copper is highly susceptible to cavitation attack (2003). They noted that vaporous cavitation should not be occurring in domestic water supplies. Gaseous cavitation may be the actual cause of pipe failure in these circumstances. In addition, recent forensic evaluations of some failed copper pipe sections revealed a damage pattern consistent with that believed to be cavitation implosion (Figure 1-18).

Figure 1-18. Pipe from a Real Premise Plumbing System Exhibiting Possible Cavitation Bubble Implosion Damage

Flashing

A lesser known phenomenon, flashing, occurs in a manner similar to cavitation but here the downstream pressure does not quickly rise above water's vapor pressure; i.e., the vapor bubbles generated stay intact and do not immediately collapse. The fluid flowing downstream is a mixture of liquid and vapor (i.e., a two phase system) at high velocities, and gives rise to potentially explosive and certainly hazardous heterogeneous clouds, often resulting in erosion of downstream piping (Cleary et al. 2007, Skousen 2011). Figure 1-19 demonstrates the pressure curve differences for both cavitation and flashing.

Flashing can occur in any configuration of liquid – whether static, like in a pressure tank or flowing, as being ejected through some configuration into a low-pressure region (Brown and York 1962). In fact, flashing is used in aerosols manufactured for industries,

agriculture, and household purposes (Kitamura et al. 1986). For liquids flowing through pipes and nozzles, rapid depressurization brings the liquid from subcooled to saturated and finally to superheated state initiating bubble nucleation, which then increases water volume (i.e., bubbles contribute to surge in void fraction), and can subsequently lead to cavitation damage downstream (Watanabe et al. 1996; Riznic et al., 1987; Elias and Chambre, 2000). Flashing is encountered in boilers and steam generators, converging-diverging nozzles, containment failures that leak hazardous chemicals into the atmosphere, and nuclear power plants with supersaturated waters (Shin and Jones 1986, Elias and Lellouche 1994, Witlox et. al, 2006). Flashing can also occur in piping systems with valves where bubbles form in the vena contracta immediately following the valve and cause downstream erosion (Kitamura et al. 1986). The location within a flow where the liquid begins to flash is called the 'flashing inception point'.

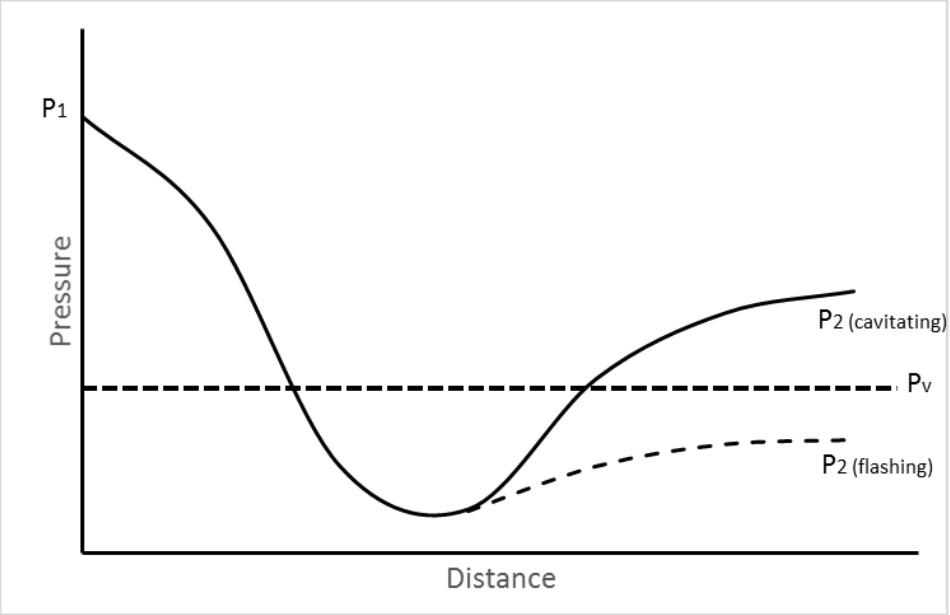

Figure 1-19. Pressure curves for cavitation and flashing where P_1 is upstream pressure, P_2 is downstream pressure and P_V is the vapor pressure of the liquid Reprinted from Skousen, © 2011, with permission from Emerson Fisher.

A combination of hydrodynamic instabilities and thermal non-equilibrium conditions causes flashing where the liquid can come to a new equilibrium by releasing its superheat through evaporation which consists of boiling and vaporizing of the droplets as they disperse and provide an explosive characteristic to the process (Calay and Holdo 2007). The length of the nucleation zone for bubbles strongly depends on the flow velocity, depressurization rates and level of superheating (i.e., the temperature of vapor above water's boiling point) (Jones and Zuber 1978). Figure 1-20 is a flashing jet schematic as it occurs from a nozzle/leak but can be theoretically extended to flashing phenomena inside pipes or vessels. In terms of two-phase flow formation profile, bubbles, initially close to the wall, continue to grow and then agglomerate ultimately migrating to the core of the flow further downstream due to their (bubbles') faster acceleration compared to flowing water; this represents a sufficiently developed bubble profile controlling any

vapor generation downstream of the channel (Riznic et al. 1987). The bubbles continue expanding and accelerating downstream often agglomerating into slug bubbles and, therefore, forming a continuous vapor core towards the annular flow regime.

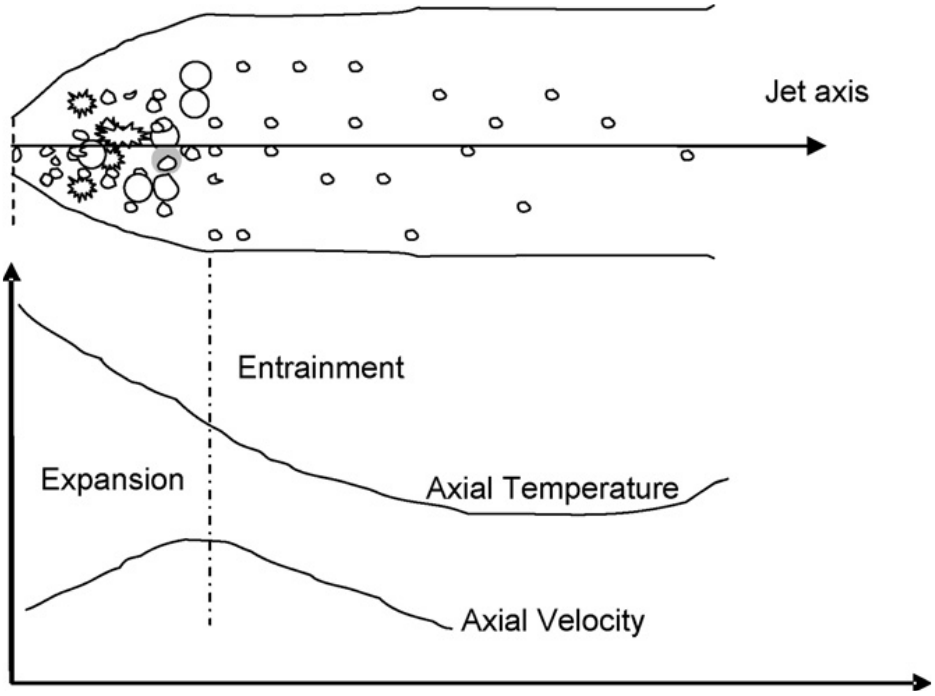

Figure 1-20. Schematic showing the expansion and entrainment region of a radially flashing jet and typical temperature and velocity variation along the jet axis. The radial variation of droplet size, temperature and velocity at different locations along the jet axis show approximate Gaussian distribution. For flashing inside pipes, the temperature/velocity curves in the entrainment region will be different owing to different hydrodynamic conditions.
Reprinted from Calay and Holdo, © 2007, with permission from Elsevier.

There are limited experimental studies for flashing in pipes carrying water (Reocreux, 1974; Seynhaeve et al., 1976; Ardon and Ackerman, 1978; Seynhaeve, 1980) that found an increase in mass fluxes causes a corresponding decrease in superheat. Moreover, at very high mass fluxes (up to 20,000 kg/m^{2}s) and temperatures of 110-167°C, flashing at negative superheat, i.e. bubble nucleation initiated above vapor pressure of water, was witnessed. The effect of pipe geometry i.e. length to diameter ratios (L/D) indicating short or long tubes and orientation has been explored to a limited extent. Fraser and Abdelmessih (2002a) moved the point of flashing inception along the length of different pipes by altering the position of a smaller diameter cavitating ring inside and found that superheat decreased as the location of flashing inception was moved upstream. A typical axial pressure profile from their experiment in shown in Fig 21. Subcooled water (at P_0 and T_0) is discharged along the pipe where local static pressure reduces with distance reaching saturation pressure P_{SAT} (at $T=T_0$), becomes superheated and ultimately flashes at location Z_{Fi} (local static pressure = P_{Fi}). The degree of superheat ΔT_S (= $T_0 - T_{SAT}$ (P_{Fi})) changes when the ring location is moved which then alters the flashing inception

point in the pipe. Based on experimental data, Fraser and Abdelmessih (2002b) developed a mathematical model that only required knowledge of upstream stagnation state and pipe geometry to predict maximum and minimum critical mass fluxes. These experiments, however, tested temperatures only above 110°C and it is unclear if such flashing two-phase (water/vapor) systems can occur in actual premise plumbing with complex flow geometries, fittings, temperatures below 70°C and varying pressure conditions along the length of the pipe.

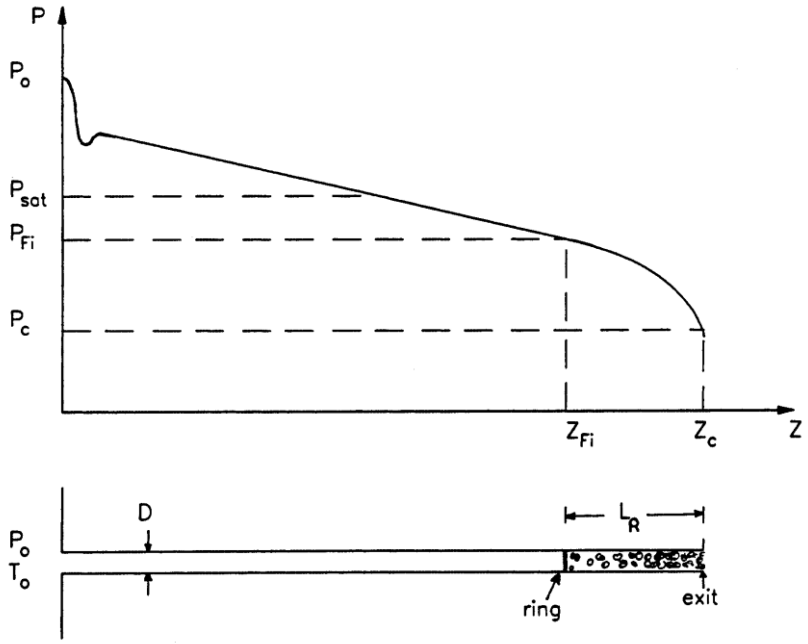

Figure 1-21. Pressure profile and flashing location for critical two-phase flow Reprinted from Fraser and Abdelmessih © 2002, with permission from Elsevier.

Despite numerous flashing models (Shin and Jones 1993, Elias and Chambre 2000, Fraser and Abdelmessih 2002b, Calay and Holdo 2007, Cleary et al. 2007, Saurel et al. 2008) and reviews (Kitamura et al. 1986, Shin and Jones 1986, Riznic et al. 1987, Elias and Lellouche 1994, Polanco et al. 2009) available, one cannot predict flashing behavior (Polanco et al., 2009). The long-term effects of flashing inside copper pipe and damage mechanisms from flashing within plumbing systems require investigation.

Particle Impingement

The formation, growth and proliferation of particles in water distribution systems is complex and not well understood. Particles can originate from a variety of sources, both external and from internal processes within the distribution system, including:

a) background concentrations of organic/inorganic material from source waters;
b) suspended solids not completely removed at the treatment plant;

c) particles added to the water at the treatment plant (like carbon and sand particles, alum or iron flocs, and bioparticles from biofilters) or forming within the distribution system via pipe and fitting corrosion, lining erosion, biological growth, or chemical reactions;
d) external contamination during pipe repairs, intrusion, or back flow.

Further complications result due to physicochemical changes during contact with different pipe materials, their ages and changing hydraulic conditions (Vreeburg and Boxall 2007). Particles often precipitate in water heaters from carbonate hardness containing waters (Pierre 2005). Hot water from "instantaneous heaters" or multiple tube heat exchangers in domestic systems at low velocities can allow sand particles, corrosion products and/or organic matter from the water supply to settle out in the pipes (NACE 1980). Finally, debris left inside plumbing post-installation (possibly from manufacturing, transport, storage and even during installation) can act as potential instigators of localized corrosion in copper (Schock and Lytle 2011).

Particle impingement describes the possible progressive wearing-away or mechanical breakdown of pipe material due to particle impact against the plumbing material. The terms abrasion, erosion, and wear are used interchangeably in this section to describe this phenomenon, although they carry distinct meanings in the literature of other fields. To avoid problems with erosion corrosion of copper, pipe networks are generally designed to ensure that the water velocity does not exceed about 6 ft/sec in hot water systems, but if abrasive particulates are present it is believed that failures can occur at much lower flow rates (Oliphant 2010, CDA 2016). Particulates lend slurry-like characteristics and increased abrasivity to flowing water, which, in turn, can likely shorten the life of the pipe material to a large extent. Henceforth, the term "slurry" describes particle-carrying liquids irrespective of particulate concentrations. Solid particles can damage both types of protective films, i.e. thick diffusion barriers and thin passive films, on the pipe wall leading to erosion corrosion (Postlethwaite and Nesic 2011). A generally accepted model for this simultaneous action of erosive and corrosive processes (Figure 1-22) is referred to as tribocorrosion (Stachowiak and Batchelor 2014).

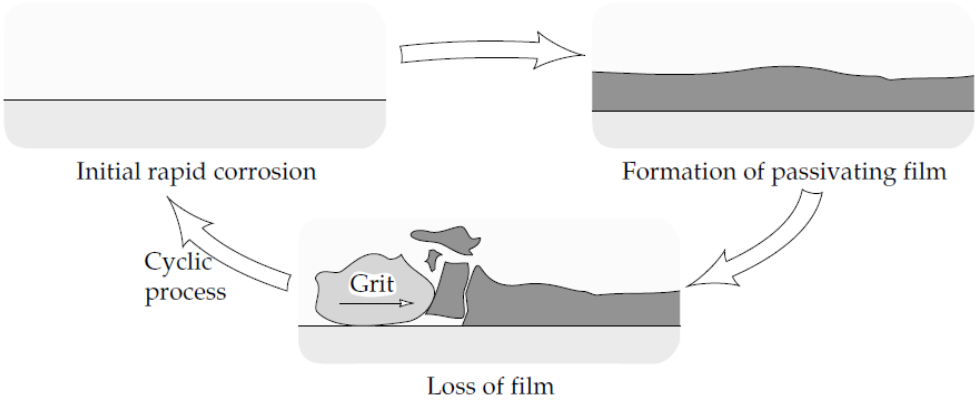

Figure 1-22. Cyclic removal of corrosion product films by abrasion
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Particles can severely accelerate damage rates as was seen in an experiment where corrosion rates in carbon steel pipes carrying water rose tenfold from 1 mm/y to approximately 10 mm/y because sand was introduced (Postlethwaite et al. 1986). Baseline corrosion rates can even be insignificant when mechanical abrasion is more intense (Batchelor and Stachowiak 1988). In other words, plastic deformation can be responsible for pure erosion damage caused due to solid particle impact (Matsumura 2012). In such high erosion prone attacks, there is progressive formation, extension, and subsequent breaking of highly distressed layers on the metal microsurface due to impingement of particles (Levy 1995).

The ASTM standard G119-09 includes tests to calculate material losses resulting from interactions between erosion and corrosion mechanisms (ASTM 2009). Specifically, it allows conducting one out of several available wear tests involving corrosion, thereby giving combined erosion and corrosion material loss rates. This is followed by a repeat of the same test with cathodic protection of the test material (which may not always be practical for water pipes) to suppress corrosion and calculate erosion-specific loss rate. The corrosion rates can then be obtained by subtracting the latter from the former. There is extensive experimental work evaluating erosion from slurries containing particles (Zu et al. 1990, Gupta et al. 1995, Stack and Pungwiwat 1999, Clark and Hartwich 2001, Zhang et al. 2007). "Erosive-abrasive" wear produced by solid particles entrained in a fluid stream has been found responsible for premature failures in industrial operations for equipment parts like oil-well casings, pump casings, stormchokes, pipe bends, condenser tubes, power plant boiler tubes, and slurry pipelines (Wahl and Maier 1952, Olesevich 1959, Tanabe 1969, Faddick 1975, Thompson and Aude 1976, Zhong and Minemura 1996). Sand particles can play a major role in erosion corrosion of oil and gas production systems (API 1990).

A thorough literature search revealed no experimental studies on the role of (abrasive) particles in erosion corrosion of copper in potable water systems, beyond a few vague recommendations in overview papers that such reactions were important (Myers and Cohen, 1998; CDA, 2009; Oliphant, 2010).

Erosion and particulates

Schleich lists particle content and their size, magnitude of impingement, flow profile, and associated water chemistry as factors that can be detrimental to the performance of copper alloys in brackish waters owing to erosion corrosion (2004). The erosion rate especially depends on the kinetic energy of particles ("the high pressure developed between the abrasive particle and the material surface"; proportional to u_p^2 where u_p being the particle velocity), and frequency of impacts (proportional to u_p) to a first approximation (Benchaita 1980, Benchaita et al. 1983, Lotz 1991, Postlethwaite and Nesic 2011):

$$\text{Material loss rate} \propto u_p^3 \qquad \text{(Equation 1-6)}$$

The velocity exponent can range from 1 to 3 depending on pipe material and particulate type (Heitz et al. 1991). Post-removal of scale, attack on the underlying metal becomes "strongly non-steady state" and, the longer the pipe wall remains exposed to flow, the larger the exponent becomes (owing to speedier wall thinning). Cavitation attacks can also increase the velocity exponent further upward to 5 – 8 (Lotz 1991) although damage due to particles can prevent detection of cavitation occurring simultaneously. At low velocities, accelerated corrosion is the major factor, whereas at high velocities, erosion can lead to rapid degradation as witnessed in oil and gas applications (Smart 1993).

Particle trajectories in liquids follow complex geometries especially when flows are turbulent and encompass a wide range of impact angles (Postlethwaite and Nesic 1993) which makes it highly unlikely that a singular impact angle always causes the worst damage. A reducer downstream of a T-junction and pinch valve subjected to sand slurries in disturbed flow conditions witnessed an extraordinary failure via erosion in an alarming eight days (Postlethwaite et al. 1978). For ductile materials like copper, the erosion corrosion maxima develops at impact angles in the range of 15 – 50 degrees. A set of experiments found maximum thickness loss at 45 and 55 degrees angles in horizontal and vertical one-inch aluminum specimens respectively demonstrating the role of flow orientation (Mazumder 2004, Heitz 1991, Schmitt and Bakalli 2010). On the other hand, in a series of of jet impingement experiments on steel alloys with slurries of both coal-kerosene and silica-water, peak erosion rates were obtained at 90 degrees with an intermediate peak occurring somewhere between 40 to 60 degrees range for many but not all alloys. According to Levy, particles most effectively penetrate the lubricating film of the carrier liquid at a 90 degree angle, transmitting maximum impact force on the wall surface, and, hence, peak rates would likely be observed at this angle (1995).

Schleich's (2004) "particle content and size" description includes particle density, size, shape, terminal velocity, micro-roughness and solids concentration (Tanabe 1969, Wilson et al. 2006, Postlethwaite and Nesic 2011). The force of particle impact is proportional to mu_p, and so the effect of smaller/less dense/softer particles will be rather small. Larger and more angular particles tend to be increasingly abrasive while higher particulate concentration causes enhanced corrosion (Schleich 2004, ASTM 2013). While particulate shape is not representative of its surface micro-roughness, their combination influences the forces generated on the pipe wall on impact. As evidenced by erosion experiments with both round sand and glass particles, erosion rates in the sand condition were two orders of magnitude greater owing to their surface micro-roughness (Postlethwaite and Nesic 1993). Studies have also shown that the "particle size effect" is not necessarily a factor above a critical value under the same test conditions – usually observed between 100 – 200 μm (Tilly and Sage 1970, Stack and Pungwiwat 1999). Damage rates drop significantly when particle sizes are below 100 μm (Glaeser 2005).

Finally, the impact frequency and erosion rate are proportional to the solids concentration in dilute slurries with less than 5% volume solids (Blatt et al. 1989). This dependency is reduced at higher concentrations due to particle-particle interference. Increased solids loading can greatly accelerate erosion despite associated increase in viscosity of the slurry liquid as seen in the coal-laden kerosene slurry experiments in a slurry pot tester on

steel alloys (Levy et al. 1987, Levy and Hickey 1987). Erosion rates decreased for some steel alloys but not others with increase in temperatures – a phenomenon that cannot be readily explained; the rates eventually rose back up at even higher temperatures (>100°C). Finally, the cumulative erosion rates decreased with time in a short run of five hours leading the researchers to conclude that initial impingement caused "the surface to be deformed to a smoother microstructure which led to fewer exposed platelets that could be struck and fractured by impacting particles" and this presumably retards erosion (Levy 1995).

Erosion drops dramatically when impacting particles are softer than the wall material (Finnie 1960, Wasp et al. 1977, Kosel 1992, Schmitt and Bakalli 2010). In other words, if a slurry with particulates of Mohs hardness 3 were flowing in a pipe of Mohs hardness 5, the particles could possibly damage rust films and cause accelerated corrosion but would not significantly cause erosion of the underlying metal (Postlethwaite and Nesic 2011).

When a fluid stream containing solid particles is turned as in pipe bends or tees, the particle trajectories deviate from that of the fluid: almost all solid particles are thrown against the outer wall due to centrifugal forces (Benchaita 1980). Hence, for relatively coarse particles passing through bends, tees, contractions of pipes, projecting nozzles, erosion on these surfaces are very severe. In straight lengths of piping, extreme conditions occur whether solids are transported mainly in state of suspension or slide, roll and jump at the bottom of the pipeline (Goldstein 1938).

It is important to point out gaps with current erosion wear models for solid particle impingement in terms of representing relevant variables. Meng and Ludema shortlisted 28 models of erosion wear via solid particle impingement and found 33 parameters amongst them. The average number of parameters per model was five, and there was no consistent pattern of parameter use and no single equation containing all 33 parameters (1995). Several cherry-pick variables for their word models and empirical equations and "arbitrarily […] emphasize [those variables'] role in the overall erosion phenomena" while others make "no pretense towards developing fundamental concepts" but do sometimes provide (valuable) data from specific testing mechanisms (Benchaita 1980; Meng and Ludema 1995). This seemingly vast number of variables also underscores the complexity of testing methods like the G75-07 standard used for abrasive and/or corrosive slurries.

ASTM Standard G75-07 is used to determine the relative abrasivity of a slurry owing to constituent particulates called the "Miller Number." This number is calculated with respect to weight losses in a "standard" 27% chrome iron wear block rubbed in that particular slurry with a 50% solids concentration by weight for a specific amount of time (Miller 1995, ASTM 2013b). Miller numbers for different samples of a particular copper ore are listed in Table 1-7. Pitting corrosion in copper primarily caused by considerable oxygen (air) present in the slurry due to agitation both in Miller equipment and actual pumps leads to a great deal of metal loss and thus contributes to a higher Miller number. Tests done at higher pH by dosing sodium hydroxide (NaOH) severely suppress the

corrosion effect, making it possible to quantify the abrasion rate almost alone. Since the Miller number is primarily focused on slurry abrasiveness with respect to a "standard" metal type, it does not explicitly consider the role of 'relative hardness' i.e. the role played by hardness values of both the particulates and the metal on which impingement occurs.

Table 1-7. Miller numbers for various samples of a copper ore (Miller 1995, ASTM 2013b)

Sample	pH	Miller Number
No. 1	6.3	92
No. 2	1.3	553
No. 3	5.9	117
No. 3 NaOH inhibited	13+	33

There also exists a "paucity of good experiments to verify proposed models" (Meng and Ludema 1995) which is further convoluted by an excess of models flooding the literature making it difficult to either choose models to design experiments for or vice-versa. More than a decade after Meng and Ludema (1995) pointed out shortcomings of erosion models, mechanistic models and empirical correlations have continued to be published for estimation of erosion wear based on experimental data obtained through laboratory test rigs. Take this equation from Desale and colleagues (2008) as an example:

$$E_w = K\, V^{\beta}\, d^{\gamma}\, C^{\phi}\, f(\alpha) \qquad \text{(Equation 1-7)}$$

where E_w is the erosion rate, V the velocity; d the particle size; C the solids concentration; K, β, γ and ϕ are constants whose value may be a function of the material properties of solids, target and carrier fluid. The values of the constants varied over a wide range because of differences in the experimental conditions and materials used (Desale 2008) and, thus, no universally accepted correlation exists for estimation of wear. For this study, the erosion wear has a strong dependence on velocity, particle size, relative hardness (for normal impacts) but relatively weak dependence on solid concentration. Clearly, efforts towards a unifying model or, at the very least, an overarching representation (and mapping the relative influence) of these variables have come up short and there is confusion about what factors are most practically relevant.

Relative Hardness and erosion mechanisms

The extent of abrasive wear occurring on the pipe material will depend on the ratio of the hardness of the particle to the hardness of the pipe surface being worn (Wahl 1951, Wellinger and Uetz 1955, Uetz and Föhl 1969). This ratio of particle hardness to that of pipe is termed as "Relative Hardness" (or, "Hardness Ratio"). Consider the hardness of graphite (Mohs hardness ~ 2) and silica sand (Mohs hardness ~ 7) particulates relative to that of copper (Mohs hardness ~ 2.5-3). If erosion via impingement is the dominating mechanism, it can be expected that copper will be abraded more readily and rapidly by silica sand than graphite particles. According to one set of experiments, abrasive particles of material A will scratch material B if the hardness of A is at least 20% higher

than that of B on the Vicker's scale (Akagaki and Rigney 1991, Rigney 2000; Pintaude 2010). Feng and Ball, on the other hand, believed that the hardness of particles itself had little effect on wear as opposed to their shape and kinetic energy for ductile materials but their findings were based off gas blasting experiments in the absence of water (1999). The microstructure of pipe material also influences its resistance to erosion (Zum Gahr 1987).

From a metallurgical point of view, copper responds to *sliding abrasion* where particles move tangentially along the pipe wall and *solid particle impact* where erosion occurs by plastic deformation, micro-machining and cutting often at an angle (Benchaita 1980, Wilson et al. 2006).

In *sliding abrasion*, the normal stress is greatly enhanced when flow streamlines are curved (e.g., at elbows) and result in centrifugal acceleration proportional to u^2/r where u = local velocity and r = radius of curvature of streamlines. Curved streamlines increase wear rates which occasionally manifests as accelerated wear of elbows even though adjacent straight sections of pipe are completely unaffected (Wilson et al. 2006). Such failures can also be instigated by soft abrasives i.e. particles that are less or equal in hardness to the attacked pipe walls. The attack of such soft abrasives may result in elastic or plastic deformation, surface fatigue, surface cracking and adhesion. Protuberances due to plastic deformation of the rubbed surface may be cut or repeatedly pushed aside by following abrasive particles. Frequently the main difference between erosive wear at small attack angles and abrasive wear lies in the kinetic energy transmitted to the stressed surface which mainly affects the elastic and plastic deformation of the wearing solid (Zum Gahr 1987).

In *solid particle impact* mode, particles strike the pipe surface at varying angles and material comes off owing to small scale deformation, cutting, fatigue cracking or a combination of these. Figure 1-23 visually depicts the failure mechanisms as a consequence of solid-particle impact which typically occur because "trajectories of individual particles do not follow the streamlines of the average flow" (Wilson et al. 2006). Moreover, corrosion products sticking to the pipe walls are typically soft and loose that can come off owing to particle impacts as illustrated in Figure 1-22. Highly turbulent flow regimes often push particles towards flow boundaries along the pipe due to the action of eddies and can cause damage in the upper portions of pipelines. (Wilson et al. 2006).

Zum Gahr uses the terms "microploughing" and "microcutting" to frame dominant interactions in erosion (1987). In microploughing, prows form ahead of the abrading particle and the material is continually displaced sideways to form ridges adjacent to the groove produced. Microcutting involves material loss due to repeated ploughing by many abrasive particles acting simultaneously or successively and eventually leading to microfatigue (Buttery and Archard 1970-71, Murray et al. 1979, Moore 1979). Microcutting occurs when attack angle of the harder abrasive particles is greater than a critical angle α_C (Mulhearn and Samuels 1962, Sedricks and Mulhearn 1963, Sedricks

and Mulhearn 1964). In practice, a gradual transition from microploughing to microcutting is observed with increased attack angle (Zum Gahr 1987).

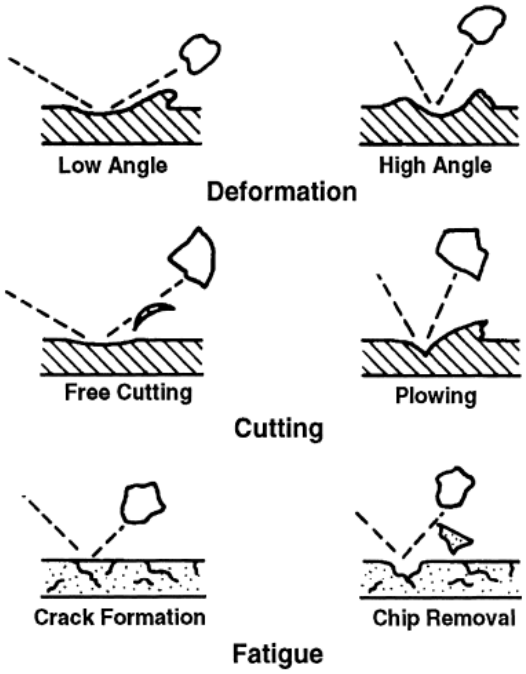

Figure 1-23. Mechanisms of particle impact erosion
From: Slurry Transport Using Centrifugal Pumps, Chapter 11 – Wear and Attrition, 3rd edition, 2006, Page 251, K.C. Wilson, G.R. Addie, A. Sellgren, and R. Clift © 2006 Springer Science-I-Business Media, Inc. With permission from Springer.

Finally, attrition is an unavoidable consequence of particulates moving continuously in pipelines and pumps, which is likely in hot water recirculation systems. Particles will get ground up, act as a carrier fluid for the larger particles (Wilson et al. 2006) thereby reducing friction losses and altering the wear rates as the effective size and size distribution of the particles changes.

Precipitation of water hardness (Calcium Carbonate) as particulates

Water hardness (expressed in mg/L as $CaCO_3$) refers primarily to calcium and magnesium salts dissolved in water. Typically, water hardness precipitates as off-white solids called "scale" on pipe walls comprising predominantly of Calcium Carbonate ($CaCO_3$) along with Magnesium Hydroxide, Calcium Sulfate and other salts. This coating increases conductive resistance to heat transfer; not to mention, narrowing and even blocking the flow pathway (Royer et al. 2010). Precipitation to a certain degree is preferred since it purportedly forms a protective eggshell-like coating on the walls reducing chances of direct contact between the flowing water and the pipe. However, increased precipitation in the form of particulates can contribute to fouling inside the distribution system (like pipes, valves and meters) as well as consumer or industrial facilities like hot water tanks, pressure tanks, heat exchangers and boilers, and cause a

buildup of sediment when interacting with other treatment process residuals (Ranjbar 2010, Schock and Lytle 2011). Moreover, the concentrations of such solids keep increasing in constantly circulating systems (Ranjbar 2010). Langelier Index (LI) and Calcium Carbonate Precipitation Potential (CCPP) are two measures that have been used historically to predict conditions that favor $CaCO_3$ precipitation, although there is growing consensus that these indicators are always reliable, especially when scaling inhibitors are present (Snoeyink and Wagner 2011, Wang et al., 2017).

Precipitation and scale formation increase with rising temperatures; the rate of scale formation was seven times higher in a water heater system at 82°C than that of a normal domestic water heater at 60°C. Very high temperatures can be reached in domestic hot water systems – house-heating furnaces, for example, can lead to water being delivered at as high as 93°C (Krappe 1940). Moreover, calcium carbonate can deposit as either of its polymorphs aragonite or calcite especially close to the metal heating elements in water heaters at high pH values of 8.5 (Pierre 2005). Scales deposit fastest at highest heat input spots (Davies and Scott 2006) - in heat exchangers and heating elements of water heaters, for instance. In fact, high concentrations of aragonite particles and chunks were found inside copper tubes and pump impellers of hot water recirculation systems that witnessed extensive damage and leaks and were served by very hard water (Roy and Edwards 2014). Based on the above discussion, it is predicted that water hardness precipitating as calcite or aragonite particulates can have devastating consequences in copper plumbing systems but this has yet to be investigated in the laboratory.

Understanding specifically how particles exacerbate erosion corrosion of copper will complement current knowledge of "erosion" with electrochemistry to uncover synergistic effects. Electrochemical methods allow for simulation of oxidation characteristics, which are representative of a corrosive environment, offer insights into kinetics of these reactions both in situ and in real time, and aid calculation of metal removal owing to corrosion. These outcomes are critical pieces of the erosion corrosion puzzle which currently rely on wear/erosion techniques/models as well as surface characterization of affected pipe material and wear particles, to some extent (Landolt, et al. 2001, Ponthiaux et al. 2004, Mischler 2008). In 1984 Tabakoff said there was "great potential for research exists for particulate flows in turbomachinery," which still holds true for practical applications including copper premise plumbing.

'High' Velocity Water Impingement

High velocity water impingement is believed to detach copper scale from pipe walls or otherwise alter the type and distribution of scale that forms (Bengough and May 1924). It can also "disrupt formation of protective films like metal oxides, hydroxycarbonates and carbonates" which otherwise may help protect against corrosive attack (Schock and Lytle 2011).

Landrum (1989) believed that the local velocity of water can be greatly accelerated when it passes by deposits on pipe surfaces. Without citing any studies, Landrum stated that velocities can increase from 6 ft/sec (a typical premise plumbing water velocity) to 300

ft/sec just past small flow obstructions like burrs, tubercles, deposits (1989) or solder blobs (CCBDA 1997). Marshall and colleagues proved that copper pinhole leaks formed most readily at bends i.e. in areas of greatest turbulence (2004), even though copper scale was not detached. Landrum also pointed out that increasing water velocity makes protective films detached more rapidly, and that copper itself is very sensitive to increasing fluid velocities (1989). Finally, high velocities can accelerate corrosion by delivering oxidant species to the pipe walls at increased rates (Schock and Lytle 2011). Increasing velocities inside a pipe often translate into turbulent flow conditions i.e. higher Reynolds number, which in turn leads to higher shear stress on the pipe walls as well as a turbulent boundary layer near the wall. Reaching very high velocities can result in sudden pressure changes that in turn propagate vibrations, high noise levels and water hammer effects through the pipes, and ultimately damage or even burst piping supports and piping connections (Skousen 2011).

Finally, gas bubbles entrained in these high flowing fluids can damage protective scales, layers, or films when impact energy is high enough; like, at the inlet of heat exchanger tubes where air bubbles can develop a substantial radial velocity component. Such damage begins with isolated "horseshoes" which grow together and finally cause considerable roughening of the wall surface (Schmitt and Bakalli 2010). In fact, Suzuki and colleagues witnessed erosion corrosion in copper tubes carrying hot tap water with "micro-bubbles" at velocities of 1-1.5 m/s and 60°C temperature within a span of just three months as opposed to the condition without bubbles (2009). While the spectrum of studies conducted indicate the critical role velocity plays, by itself or in conjunction with other factors, finding reliable threshold velocities for copper pipes in plumbing standards worldwide (see Table 1-2) has proved elusive.

SUMMARY AND CONCLUSIONS

Based on a thorough review of the literature, the following statements can generally be made regarding flow-induced failures in copper-based potable water systems:

- Copper pipes and fittings are widely used in premise plumbing in the developed world. Premature failure of copper due to erosion corrosion has been reported widely; however, save a handful studies in the 1960s-70s, failures have not been systematically studied or recreated in the laboratory. As a result, plumbers, consultants, and trade organizations rely on deficient (often, anecdotal) evidence when inspecting pipe damage and offer preventive recommendations without supporting data.
- Conversely, erosion corrosion in seawater operations has been examined for copper-based alloys; a research-backed "critical velocity" to prolong the service life of many such alloys is available.
- Erosion corrosion typically occurs due to the interplay of mechanistic (includes hydrodynamic) and electrochemical factors from flowing water in copper plumbing; either can contribute in major fashion (even 100% in some cases) in removal of protective scale and underlying copper metal.

- Available design standards, recommendations and building codes for preventing erosion corrosion as a function of flow velocity and temperature are wide-ranging, conflicting and sometimes impractical. This makes available models and predictive equations less reliable. Moreover, current apparatuses, laboratory tests and standard methods for studying erosion corrosion are rarely commensurate to real world conditions.
- There is concern about adopting new ASHRAE guidelines on controlling Legionella growth in premise plumbing (i.e., hotter water temperatures, increased water recirculation and booster chlorine dosing) without careful consideration that these factors can themselves be instigators of flow-induced failures as was witnessed in Australia and New Zealand in the early 2000s.
- While there is no "general theory" of erosion corrosion, the "flow-induced failures" framework presented in this review compiled principal mechanisms including concentration cell corrosion, gaseous cavitation, particle impingement, high velocity water impingement and key factors (Tables 3 and 4) for scientifically studying erosion corrosion of copper premise plumbing, both in field failures and in the laboratory.

There is presently an urgent need for quality research to understand specific processes driving copper failures in potable water systems. Specifically, recreating erosion corrosion in the laboratory and generation of sound data, in light of recent ASHRAE guidelines, will help frame science-based recommendations for homeowners, plumbers, and the water industry.

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CHAPTER 2. INTERACTIVE EFFECTS OF WATER CHEMISTRY, HYDRODYNAMICS, AND PRECIPITATED CALCIUM CARBONATE HARDNESS CAUSING EROSION CORROSION OF COPPER IN HOT WATER RECIRCULATION SYSTEMS: CASE STUDY AND EXPERIMENTAL WORK

Siddhartha Roy and Marc A. Edwards

ABSTRACT

Erosion corrosion, or flow-induced failures, of copper is a complex phenomenon driven by a multitude of water quality, hydrodynamic and electrochemical factors. This most common form of corrosion attack in hot water is likely to increase with newer Legionella risk management regulations promulgating increased water recirculation, hotter water temperatures, and higher chlorine disinfectant dose. The current work reports findings from an investigation into widespread copper plumbing failure due to erosion corrosion in a large building complex, by systematically exploring the effects of relevant water chemistry and hydrodynamic variables on localized erosion corrosion attack. The results refute decades of conventional wisdom by scientifically demonstrating that hard waters are not inherently less aggressive than soft water, and in fact if calcium carbonate solids form they can become even more aggressive. Entrained particles significantly accelerated attack on copper pipe walls, especially in high turbulence areas like bends. This is the first research study to reliably reproduce rapid erosion corrosion failures in realistic potable water chemistry in the laboratory.

KEY WORDS: aragonite, erosion corrosion, copper, hot water, particle impingement, water chemistry

INTRODUCTION

Erosion corrosion, or flow-induced failures, of copper in hot potable water systems, can occasionally cause accelerated pipe damage and fully-penetrating leaks in a span of months or few years. This is drastically lower than copper pipe's conventional service life of 25-50 years and can cause costly repairs, plumbing replacement and water damage (Lewis 1999; CDA 2010). Erosion corrosion is the most commonly identified form of copper pipe failure, representing 34% of all failures in hot water systems reported to the Copper Development Association during 1975-2004 (Scardina et al., 2008).

Erosion corrosion failures are typically shiny, devoid of rust, and are identifiable because of wavelets, deep grooves, and "horseshoe" shaped pits. The most widely accepted theory underlying its occurrence involves either a mechanical attack, such as high water velocity, particle/bubble impingement or cavitation, which removes protective oxide scales from the pipe walls, and/or an electrochemical reaction between copper surfaces exposed to differential velocities (Myers and Obrecht 1972; Campbell 1982; Singley et al. 1984; Cohen 1993; Scardina et al. 2008; Oliphant 2010). A multitude of factors including velocity, temperature, pH, water hardness, entrained air bubbles/particulates, and poor workmanship, influence the initiation and acceleration of this form of corrosion. However, owing to an inability to replicate these failures in the laboratory as they have occurred in practice, definitive understanding of the interplay between these variables is lacking (Roy et al. 2018). The prevalent design standards and plumbing codes rely on anecdotal evidence and illustrate the poor existing conventional understanding. To illustrate, for velocity alone, the plumbing guidelines for maximum velocity in copper pipe circulating hot water vary from 1.5 to 5 ft/s (0.45 to 1.5 m/s). Recently, guidance emphasizing adoption of hot water recirculation systems, higher water heater temperatures (>=60°C from the current set-point 48 °C) and dosing of chlorine to minimize growth of opportunistic pathogens, especially Legionella pneumophila, is being adopted in the U.S (ASHRAE 2015). Similar practices implemented in Australasia led to a significant rise in erosion corrosion failures more than a decade ago (Nicholas and Gates 2012).

Except a few landmark case studies in the 1960-70s (Obrecht and Quill 1960a-f, 1961; Knutsson 1972), practical progress in understanding erosion corrosion of potable water systems in laboratory studies has been virtually nonexistent. The conventional wisdom is that rapidly flowing (often, turbulent) and heated soft waters are most likely to instigate failures, and hard waters were almost never problematic. Two scholars, based on field experience, created mathematical equations to predict penetration rates relying on three factors: a) hard v/s soft water, b) reamed v/s unreamed pipe cut ends and c) whether temperatures were above or below 60 °C. Circulating hot water systems built using pipes with unreamed ends and carrying soft waters over 60 °C were designated as the "worst case" scenarios for accelerated erosion corrosion (Myers and Cohen 1998). However, these overly simplistic equations were not backed by any available data, did not include any role for water velocity, pH or dissolved oxygen which are believed to be controlling factors. This illustrates the poor state of current knowledge regarding the cause(s) of these failures.

Recently, Coyne (2009) successfully replicated erosion corrosion damage using heated seawater by combining the phenomena of cavitation, concentration cell corrosion and high velocity impingement, but like other researchers, was unable to replicate rapid erosion corrosion in potable waters with these factors. Coyne and others have hypothesized that particle impingement due to abrasive solids entrained in flowing water could attack pipes in potable water (2009). These particles can originate from a variety of sources, including from the distribution system, corrosion of steel hot water heaters/storage tanks, or precipitation of calcium carbonate scales in water heaters of premise plumbing. Two calcium carbonate polymorphs, calcite and aragonite, may be especially important in such systems (Pierre 2005; Ranjbar 2010; Schock and Lytle 2011; Roy et al. 2018).

Most available erosion corrosion testing methods do not replicate real-world fluid flow and water chemistry conditions, and extrapolation from these data are not always reliable. The ideal testing method would involve mimicking field conditions and create unambiguous damage consistent with observations in the field, but such large scale studies are cost and would not allow identification of underlying mechanisms causing failures (Sarver 2010).

In this paper, we describe a forensic evaluation of serious erosion corrosion damage caused by short-term (~18-48 months) exposures occurring in a large new building in the San Francisco Bay Area. Follow-up bench scale and pipe-loop experiments, was eventually successful in replicating these failures, and in the process shed light on the role of pH, velocity, temperature, water hardness, natural organic matter, nitrates, dissolved oxygen, entrained particles, particle size, pipe location, and disinfectants in this type of attack.

CASE STUDY: INVESTIGATION OF ACCELERATED COPPER PIPE FAILURES IN A LARGE BUILDING COMPLEX

A large new building (hereafter referred to as Building X) was subject to hundreds of copper pipe leaks within 48 months of installation. The failures were unusual in that, while some damage occurred at joints, a remarkably high fraction of the failures occurred in long, straight sections of copper pipe at velocities that rarely (if ever) exceeded 8 ft/s (2.4 m/s). The leaks were extremely problematic for the building occupants, because they caused water damage, staining and mold growth on ceiling tiles and drywalls, service interruptions during repairs. The specifics of the case prompted considerable interest and motivation for follow-up experimentation.

Finding #1: The severe erosion corrosion occurred in a system with extremely hard water (~390 ppm).

All prior scientific literature suggested that erosion corrosion failures occur more readily in soft water. It was hypothesized that rapidly flowing soft water mechanically removes any protective surface films (scales) that leave bare copper metal fully exposed and

corroding at an excessive rate (Obrecht and Quill 1960a-f; 1961 and Murakami et al. 2003).

It has been hypothesized that hard waters are seldom corrosive because very protective films form rapidly if calcium compounds are present (Sequeira 2011), although, other than the landmark work of Obrecht and Quill cited earlier, actual field data proving that soft water is more corrosive than hard water is lacking. Myers and Cohen (1998) utilized their experience evaluating over 100 field failures to develop empirical equations predicting erosion corrosion rate where soft water causes the worst damage. Another assertion is that when waters with appreciable temporary hardness are softened, they can become aggressive if heated above 140°C. It was stated that this was because the absence of calcium compounds prevents protective film formation and sodium bicarbonate formed breaks down releasing carbon dioxide, although it is also obvious that such a change results in formation of calcium carbonate precipitates (Sequeira 2011).

In addition to water hardness, the major factors believed to exacerbate erosion corrosion include excessive flow velocities, high temperatures, low pH, presence of organic matter, presence of abrasives/particulates/gas bubbles, gas bubble cavitation, and poor workmanship (Bengough and May 1924, Obrecht and Quill 1960a-f, Obrecht and Quill 1961, Knutsson et al. 1972, Cohen and Lyman 1972, Myers and Obrecht 1972, Kristiansen 1977, Myers and Cohen 1998, Novak 2005, Scardina et al.2008, Oliphant 2010, Gates 2012).

Finding #2: The hard water generated high concentrations of particles upon heating that clogged the plumbing system and might physically abrade copper.

Cold water samples from Building X were heated up to 48 °C (118 °F), which caused a large volume of white particulates to form immediately due to precipitation of calcium carbonate (Figure 2-1). The resulting heated water was essentially a dilute limestone ($CaCO_3$) slurry. Modern hot water plumbing systems are not designed to operate in very hard and high pH waters such as that present at Building X — attempting to do so can be expected to cause rapid system failures from pipe blockage, poor heat transfer and plumbing device clogging. This is consistent with consumer experiences in this building with fixtures clogging almost immediately after occupancy.

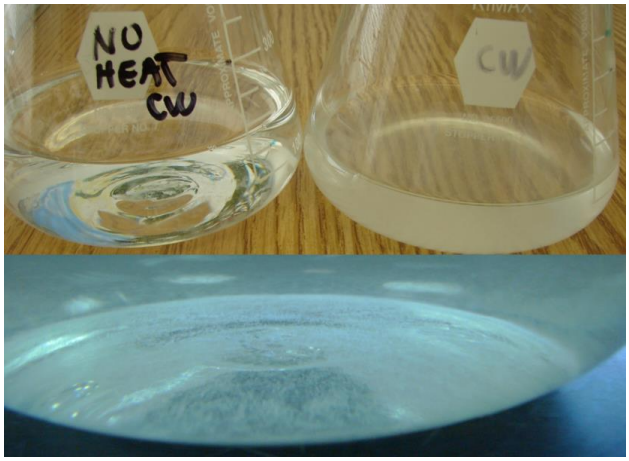


Figure 2-1. Cold water collected from Building X (upper left) generated a massive amount of calcium carbonate particulate matter when heated and was visible as white turbidity (upper right). These particulates settled and coated the glass container (lower).

Finding #3: The cause of the failures is erosion corrosion, due to excessively high water velocity (8 ft/s), and exacerbated by the presence of abrasive particulates and/or bubbles.

Over 100 copper pipe samples in a viewing area were examined during a site visit in 2011. All evidence of interior damage was clearly recognizable as erosion corrosion (Figure 2-2). This type of attack is usually caused by excessive water velocity and/or localized turbulence. Recommendations from literature and plumbing standards endorse 4-5 ft/sec as the maximum velocity for copper pipe networks carrying hot water (Obrecht and Quill 1961, CCBDA 1997, Myers and Cohen 1998, ASM 2005, PHCC NSPC 2006, CDA 2010). However, if abrasive particulates and/or bubbles are present, copper pipe is known to fail from erosion corrosion at much lower velocities (CDA 2010, Oliphant 2010).

Figure 2-2. Every sample in a viewing area (left) was examined and all significant internal pipe damage was caused by characteristic erosion corrosion (right).

Samples of a highly crystalline and abrasive particulates were removed from the pipe network (Figure 2-3), and upon analysis, these particulates were chemically indistinguishable from the ones that clogged aerators removed from the buildings (Figure 2-3). These particulates from the pipe system were much harder and larger than the small soft calcite solids that were first formed upon instantly heating the water (Figure 2-1). Three aerators inspected at the site were clogged with these particles (diameter >1 mm) and even bigger particles were photographed (Figure 2-4) when the system was being dismantled and replaced with new copper pipe. The large $CaCO_3$ particles were confirmed by X-Ray Diffraction Analysis to be aragonite, the hardest polymorph of $CaCO_3$ with Mohs hardness ~4.

The potential long-term damage incurred to plumbing systems by entrained hard particles is relatively well-understood. For example, public education materials directed at homeowners by the Water Quality Association (WQA) notes that: "Water softening is the removal of calcium and a few other minerals that can cause our working water to damage household property. When it deposits as scale, calcium carbonate (limestone) is an abrasive rock like mineral." (American Water Texas, n.d.) There are also dozens of professional and scientific reports in the literature documenting severe degradation of pipes and pumps if abrasive particles are present (e.g., Hint, 1952; Wahl and Maier, 1952; Olesevich 1959; Sheldon and Kanhere, 1972; Faddick, 1975; Mills and Manson, 1975; Thompson and Aude, 1976; Benchaita et al. 1983; API, 1990; Carter et al. 1991; Smart, 1991; Gupta et al. 1995; Miller, 1995; Klemm, 1999; Stack and Pungwiwat, 1999; Clark and Hartwich, 2001; Postlethwaite and Nesic, 2011).

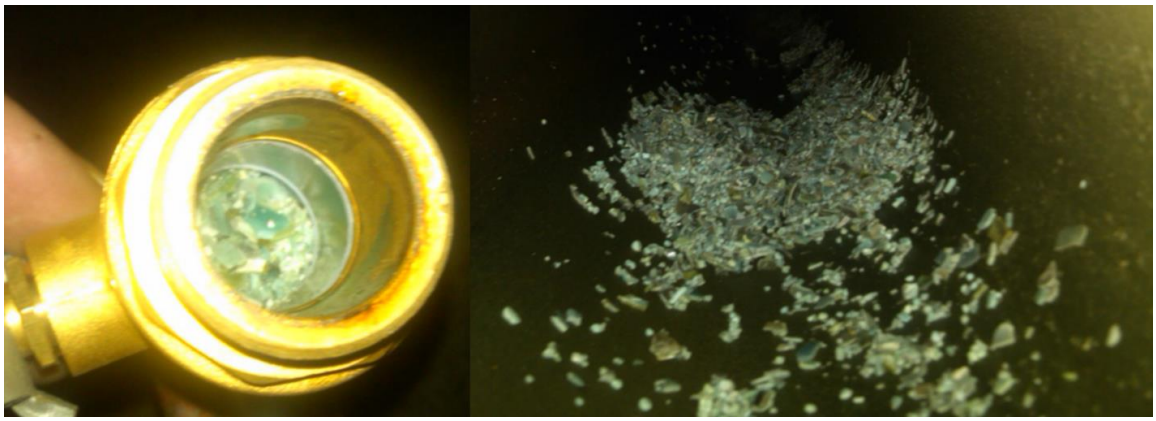


Figure 2-3. Photographs of crystals in a brass valve (left) and in a 4" cold water blow down line (right).

Figure 2-4. Very hard particulates clogged aerators (left) with very abrasive and highly crystalline calcium carbonate particulates (right). Particles on right represent only a portion of those actually present in the aerator.

Finding #4: Failures are not limited to the most susceptive portions of the copper pipe network downstream of valves and bends and flow constrictions, but instead, occur with very high frequency on long straight lengths of copper tube.

The pipe samples analyzed in the field consistently demonstrated very good workmanship and all the joints observed were properly reamed. However, numerous long straight lengths of pipe often exhibited very severe attack. In some cases severe erosion corrosion was observed more than 15 feet from the nearest valve, bend or flow constriction, which is unambiguous evidence of extremely high water velocity and/or erosion corrosion exacerbated by particles or bubbles. For one sample in which orientation could be clearly established (Figure 2-5), as opposed to others which weren't marked, erosion corrosion was much more severe along the bottom and sides of the tube than along the top. This pattern of attack is often associated with high concentrations of particulates passing through the copper pipe, settling to the bottom, and scouring the lower surfaces at high velocity while leaving the top of the pipe unaffected.

Figure 2-5. Substantial fraction of failures occurred at bends (upper center) or just downstream of valves (lower center); a very large number of failures occurred along

straight sections (left). In one case where orientation could be determined the top section of pipe had the least attack (right).

Finding #5: Most failures were not due to either faulty installation or construction practices.

Poor installation practices (improper reaming) and local turbulence (exacerbated by bubbles/particulates) due to presence of burrs, at bends (i.e., 90° or 45° bends), or downstream of valves, can also contribute to erosion corrosion but within a few inches of these locations. The fact that the pipes were attacked with a very high frequency in long straight runs of copper tube, suggest that entire sections of the pipe network were subject to extreme conditions of erosion corrosion and aggressive water. In such situations copper plumbing downstream of bends, joints and valves, will also fail with very high frequency, even if properly installed.

Finding #6: The Large and Abrasive Particles are Formed Rapidly at Higher Temperature and Pressure.

A relatively unique aspect of Building X was that steam-fired instantaneous water heaters were used at high pressure) and there was no storage in which large particles could be settled from the system. It is estimated that the surface temperature of the steam heater was over 175 °C. It was hypothesized that the large aragonite particles would be formed preferentially at higher temperatures and pressures. To test this, a specialized pressure cooker was obtained that was capable of achieving internal temperatures of 132-140 °C. The solids formed in simulated, hard Building X water at this temperature over a 4 week time period were large crystalline solids as confirmed by x-ray diffraction to be 98% aragonite and 2% calcite (Figure 2-6). In contrast, solids formed in the exact same water at either 60 °C or 97 °C were a soft paste comprised of 100% calcite (Figure 2-6). The large crystalline solids formed at higher temperature and pressure were very abrasive to copper, whereas the solids formed in the control experiments at lower temperature were not. This experiment demonstrates that the heater design and operation can influence the quantity and type of calcium carbonate solids that may form in a system, which in turn may influence its susceptibility to cause erosion corrosion.

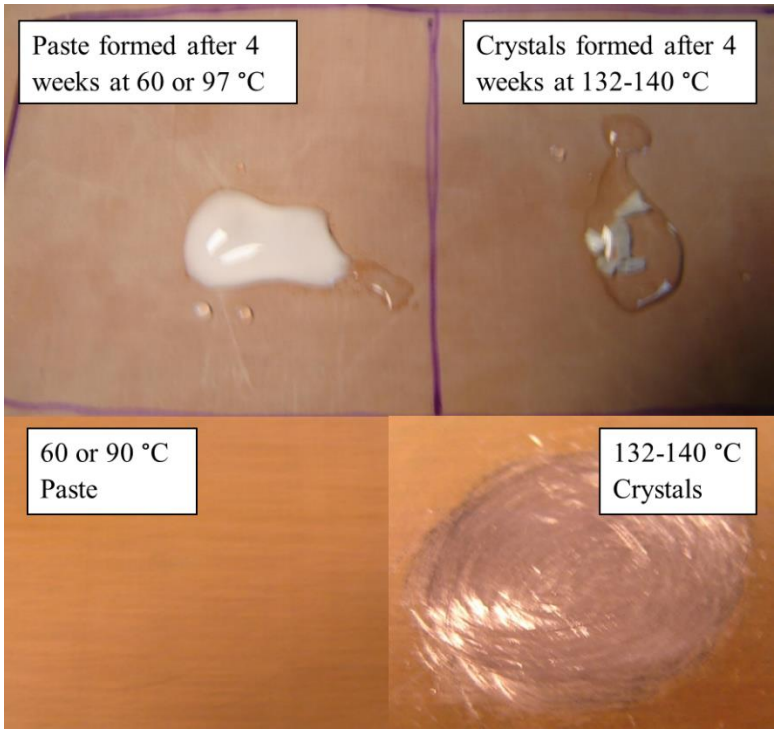


Figure 2-6. Simulated Building X water formed a soft paste when heated to either 60 °C or to 97 °C at 1 atm. pressure (upper left), but formed large hard crystals in the same test at higher temperature (upper right). When piece of pine wood covered with a soft cloth was placed on the solids, and rotated 400 times in a dime size circular motion, the copper was severely abraded under by the hard crystals formed at higher temperature (lower right) but not at all by the solids formed at lower temperature (lower left).

It is suspected that this very hard solid rapidly abraded the copper tube throughout the building (Figure 2-2), consistent with experiences of rapid pipe failure reported for crystalline limestone suspensions in other industries (e.g., Klemm 1999). Overall, the field observations were highly inconsistent with prior hypothesis that hard water would not be susceptible to erosion corrosion. The findings from this case study prompted a series of experiments described in this paper.

Review of past copper erosion corrosion failures in the geographic location surrounding Building X.

A review of copper erosion corrosion failure reports between the 1960s and 1990s from the CDA database (Scardina et al. 2008) that occurred in the same geographic location (San Francisco Bay Area) as Building X indicate a variety of field failure mechanisms, mostly in hot water systems, carrying (sometimes softened) water at very high temperatures. For example, a 17-building complex with circulating hot water systems, witnessed 60+ leaks in 5-6 years in long straight sections of pipe with velocities between 1-9 ft/s. In another instance, water temperatures for softened water reached 140 °F (60 °C), and sometimes 160 °F (71 °C) and this was deemed partially responsible for pinhole

leaks. In contrast, for softened cold water systems in a 1000-residence community, suspended solids (either from source water or corrosion from galvanized steel pipes) deposited on "bottom halves of lower tubes" causing leaks between 3.5-12 years in 19 buildings. Even anecdotally, hard waters do not seem to cause erosion corrosion failures, in sharp contrast to what was witnessed in Building X.

EXPERIMENTAL PROCEDURES

Based on a thorough literature review (Roy et al. 2018) and findings from the Building X case study, three phases of experiments were executed. The first experiment (Experiment #1) involved long term hot water recirculating systems with high velocity jet impingements on copper coupons (bench scale) to investigate effects of water hardness, pH, temperature, natural organic matter, ammonia and nitrate on copper erosion corrosion and systematically identify the worst case water chemistry (or "recipe") responsible for accelerated damage. The second experiment (Experiment #2) consisted of a large scale copper pipe-loop apparatus with Experiment #1 water recipe and suspended particulates to probe differences in copper erosion corrosion in relation to particle size, air bubbles, and presence of dissolved oxygen. The final experiment (Experiment #3) was a short-term beaker test to re-probe relevant chemistry and mechanistic factors from Experiments 1 and 2 and provide statistical validity to prior observations.

Experiment #1: Long Term Bench Scale Jet Impingement in Hot Water Recirculation Experiments

Water samples collected from the Building X were analyzed on a Thermo Electron X-Series Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) for major cations and anions. These and supporting physicochemical water analysis from a third-party analytical firm were used to determine the baseline chemistry of this hard water (Table 2-1) and prepare a synthesized laboratory version of the hard water, as well as a version in which calcium and magnesium hardness was replaced by sodium. These synthetic potable waters were prepared for experiments and changed weekly.

Table 2-1. Building X water chemistry

Parameter	Unit	Target Value
Total alkalinity	mg/L as $CaCO_3$	290
Hardness	mg/L as $CaCO_3$	390
Calcium	mg/L	85
Magnesium	mg/L	44
Sodium	mg/L	37
Chloride	mg/L	49
Sulfate	mg/L	66
Nitrate	mg/L as NO3-N	5-5.5
Ammonia	mg/L as NH3-N	<0.027

Sixteen bench-scale hot water recirculating systems (in three phases; Table 2-2) with 4 gallon polypropylene reservoirs, 1/12 HP centrifugal pumps (Little Giant, Fort Wayne, IN), and ¾" CPVC pipes and fittings (Grainger-approved brand, Lake Forest, IL) as shown in Figure 2-7 were constructed. Coupons of 2.5" length were cut (Figure 2-8) from commercially available 5' Type M 5/8"-dia copper pipes for use as test samples. Immersion heater rods of 400W rating (Glo-Quartz, Tucson, AZ) with digital temperature controllers (Ranco/ETC Supply, Delphos, OH) were used to maintain target water temperatures as appropriate. Tygon tubes of ¼" diameter were placed in-flow and ½" away from the test coupon wall to create a constant 25 ft/s (7.6 m/s) impingement jet. Water was changed weekly.

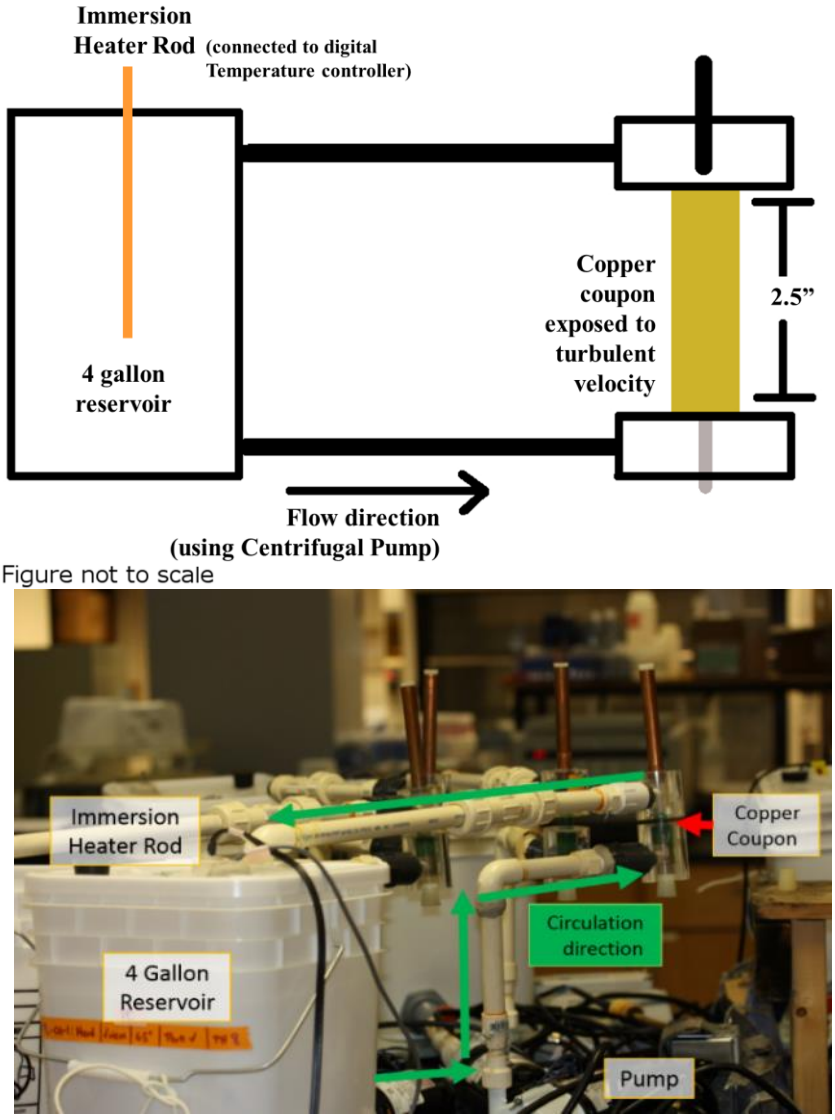


Figure 2-7. (Top) Recirculating system schematic and (Bottom) test rigs built in the laboratory

Table 2-2. Test conditions for bench-scale recirculation experiments

Test # and Condition	Run time	Details
Phase-I: Role of water hardness and pH		
1. Hard – 70 °C 2. Soft – 70 °C 3. Hard – 48 °C 4. Soft – 48 °C	48 days	Initial pH set to 8.0 Day 1-29: pH not controlled. Day 30-48: pH adjusted twice a day to 7.0 using CO2 gas
Phase-II: Role of natural organic matter (NOM), ammonia and nitrate		
With NOM (1-2 mg/L): 5. Hard – 65 °C 6. Soft – 65 °C 7. Hard – 48 °C 8. Soft – 48 °C Without NOM (control): 9. Hard – 65 °C 10. Soft – 65 °C 11. Hard – 48 °C 12. Soft – 48 °C	204 days	pH = 7.0 (adjusted twice a day using CO2 gas) On Day 65: Ammonia and Nitrate added to all conditions On Day 108: Conditions 8, 10, 11 and 12 were discontinued because no significant weight or thickness losses were witnessed
Phase-III: Role of ammonia v/s nitrate		
With NOM (1-2 mg/L) and at 65 °C: 13. Hard - Ammonia 14. Hard - Nitrate 15. Hard – Ammonia and Nitrate 16. Hard - Control	85 days	pH = 7.0 (adjusted twice a day using CO2 gas)

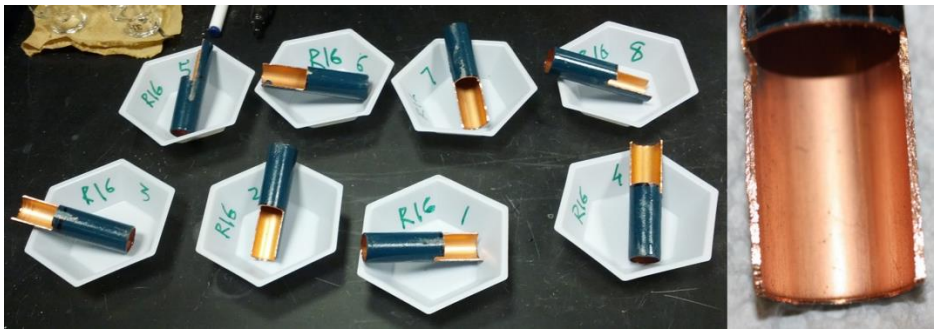


Figure 2-8. Representative copper coupons used in Experiment #1 test rigs

As shown in Table 2-3, Experiment #1 was conducted in three phases. Based on results from Phase-I, the literature (Kristiansen 1977, Francis 1985, Broo et al. 1988, El-Egamy 2004) and Building X water chemistry, natural organic matter, and later, ammonia and nitrate were introduced in Phase II. The tests with NOM were run for 204 days, and from Day 65 onwards ammonia and nitrate were added to all waters. In Phase III, experiments were conducted to isolate impacts of ammonia and nitrate on progression of erosion corrosion damage, if these ions were present from the start of the experiment.

Experiment #2: Large Scale Pipe-Loop Hot Water Recirculation Experiments

Recirculating pipe-loops of ¾ in copper pipe and copper elbows (Figure 2-9) were constructed using either Gorilla Epoxy Glue (Gorilla Glue Company, Cincinnati, OH) or Just-For-Copper Cold Solder (Highside Chemicals Inc., Gulfport, MS) of dimensions 10 ft x 10 ft (3 m x 3 m) and, later, of (vertical x horizontal) 4 ft x 5 ft (1.2 m x 1.5 m) for conditions described in Tables 2-3 and 2-4 respectively. The 10 ft x 10 ft test loop was a "proof of concept" test and the results informed further testing of the smaller pipe-loop (Table 2-3). Test water (see Table 2-5 for chemistry) stored in 5 gallon polypropylene reservoirs was recirculated using submersible pumps (Superior Pumps Model 91250 ¼ HP). Water was changed weekly.

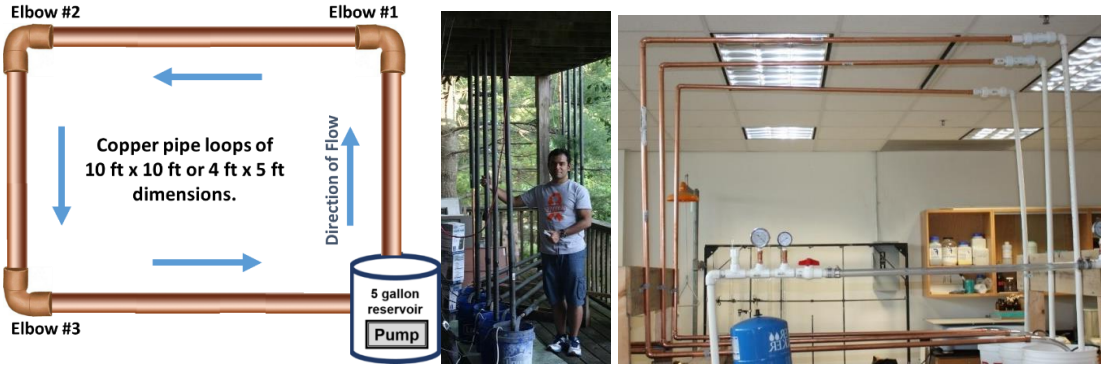


Figure 2-9. (Left) Schematic of and (Center: 10 ft x 10 ft, Right: 4 ft x 5 ft) Photos of pipe-loop apparatus for copper erosion corrosion testing

Table 2-3. Experimental conditions evaluated using 10 ft x 10 ft copper recirculation rigs – Proof of Concept

Test Name	Particulates	Associated conditions
L1 – *No Particles / Control*	–	Flow velocity: 8-9 ft/s (2.4-2.7 m/s); Temperatures 52-54 °C; pH not controlled
L2 – *Air Bubbles*	–	
L3 – *Small Particles*	Small (2 mm)	
L4 – *Small Particles + Air Bubbles*	Small (2 mm)	
L5 – *Large Particles*	Large (1 cm)	

Table 2-4. Experimental conditions evaluated using 4 ft x 5 ft copper recirculation rigs – Phase II

No.	Test Name	Particulates[#] (Aragonite, except when specified)	pH	Velocity (ft/s)	Associated Conditions
S1	*No Particles*	–	7.5	10 (3 m/s)	–
S2	*Small Particles or Low pH or High velocity or Normal*	Small (2 mm)	7.5	10	–

	Dissolved Oxygen				
S3	*High pH*	Small	10.0	10	–
S4	*Low Velocity*	Small	7.5	3-4 (0.9-1.2 m/s)	–
S5	*Low Dissolved Oxygen I*	Small	7.5	10	Sodium Sulfite
S6	*Low Dissolved Oxygen II*	Small	7.5	10	Nitrogen Gas + Sodium Sulfite
S7	*Calcite Particles*	Calcite (85% < 0.4 mm; 1% > 1.2 mm)	7.5	10	

[#] Manufacturer for particles included Premium Aquatics, Indianapolis, IN (for aragonite) and Aqua Science, Wyoming, RI (for calcite)

Table 2-5. Final hard water chemistry "recipe" determined to cause erosion corrosion and utilized in lab scale pipe-loop experiments for copper

Parameter	**Unit**	**Target Value**
Total alkalinity	mg/L as $CaCO_3$	290
Hardness	mg/L as $CaCO_3$	390
Calcium	mg/L	85
Magnesium	mg/L	44
Sodium	mg/L	37
Chloride	mg/L	49
Nitrate	mg/L (NO_3-N)	25
Sulfate	mg/L	66
Natural Organic Matter (NOM)	mg/L	1-2

For particle-based tests (Figure 2-10), relevant particulates were added at a 4% w/v concentration. For the bubbly flow scenarios, a generic aquarium air pump was utilized to inject air bubbles into flow. For lower flow velocity experiments, the velocity was reduced from the pump default of 10 ft/s (3 m/s) to 3-4 ft/s (0.9-1.2 m/s) by diverting part of the flow back into the reservoir using a ¾" PVC tee-section. For low dissolved oxygen (DO) conditions, DO levels were maintained at or below 0.5 mg/L using a) bubbling nitrogen gas in the reservoir and b) alternately bubbling nitrogen gas and dosing sodium sulfite in powdered form, three times per day.

Figure 2-10. Representative aragonite particles used in experiments alongside particles founding in Building X's plumbing

Experiment #3: Bench Scale Beaker Tests

Pure copper rods (250 um in diameter and approximately 6" length; Artistic Wire, Lillian, AL) were mounted on the inner walls of one liter glass beakers (Fisher Scientific) using alligator clamps (n=3/beaker) as shown in Figure 2-11. The beakers were filled with 1L synthetic test water (Table 2-6) and then placed on hotplate stirrers (Thermo Scientific's SUPER NUOVA Multi Plate). Rotation settings were adjusted to reach a target linear velocity of 2-3 ft/s, indicative of average water velocities witnessed in the premise plumbing. Water levels were adjusted when low (<900 mL) by adding reverse osmosis-treated water. All experiments lasted two weeks with a water change carried out at the end of Week 1. Table 2-7 describes conditions tested using this setup.

For conditions with particulates, 0.1% w/v (or, about 10 grams) of test particles were added. For experiments with disinfectant residuals, the following procedure was followed:

a) Chlorine was dosed as sodium hypochlorite from concentrated bleach (NaOCl solution stock) to achieve a 4 mg/L residual concentration (as Cl_2).
b) Chloramine was formed by dosing sodium hypochlorite and ammonium hydroxide to achieve 4 mg/L of total chlorine (as Cl_2) and 1 mg/L of ammonia (as NH_3-N).
c) Chlorine Dioxide was generated by adding 2L nanopure water to the commercially available Selectrocide® 2L500 pouch (containing 30.5% Sodium Chlorite) and target concentrations of 2 mg/L were used in experiments.

Free chlorine, total chlorine (for chloramine) and chlorine dioxide residuals were measured using a DPD (diethyl phenylene diamine) colorimetric test on a Hach Portable Spectrophotometer DR2700 as per Standard Method 4500-Cl G and 4500 - ClO_2P (for chlorine dioxide). Ammonia was measured on the spectrophotometer using the Salicylate

method as per Standard Method 8155. The disinfectant residuals were manually adjusted thrice a day.

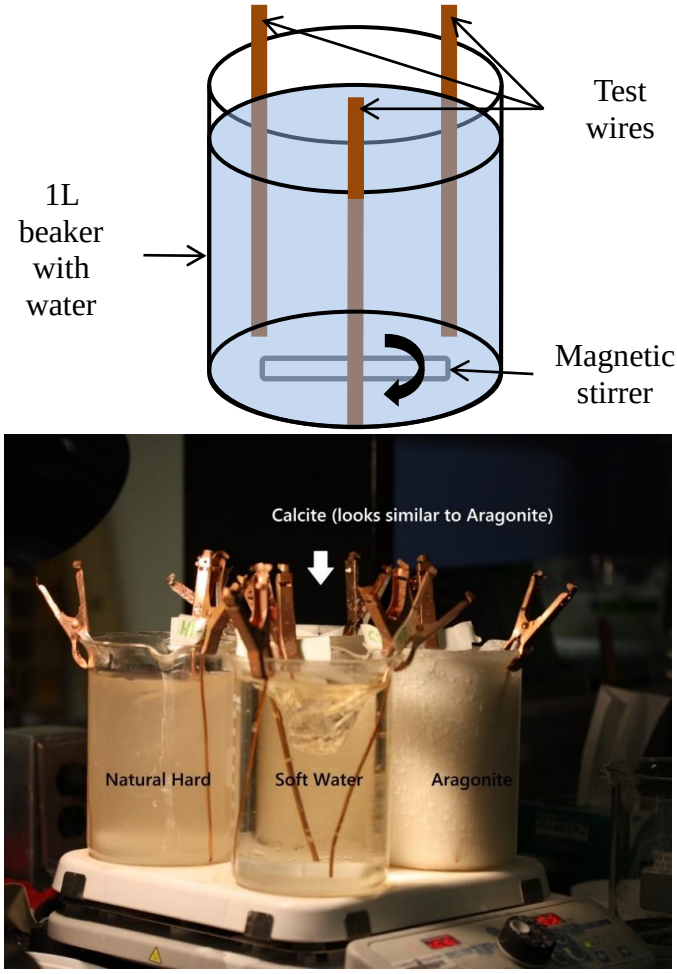


Figure 2-11. (above) Bench Scale Beaker Experiment Schematic and (below) Representative Example in the laboratory

Table 2-7. Experimental conditions evaluated using short-term beaker experiments

Test #	Water Parameter	Tested at	Associated conditions
B.1	Particulate Type	None	pH 7.5, Hard water, small particles, 60 °C
B.2		Calcite	
B.3		Aragonite	
B.3	Particulate Size	Small (2 mm)	pH 7.5, Hard water, Aragonite particles, 60 °C
B.4		Medium (4.5 mm)	
B.5		Large (1 cm)	
B.6	Temperature	48 °C	pH 7.5, Hard water, Aragonite particles (small)
B.3		60 °C	
B.7		48 °C	pH 7.5, Hard water,

B.2		60 °C	Calcite particles
B.8	Disinfectant	None	pH 7.5, Hard water, Aragonite particles (small), 60 °C
B.9		Chlorine (<4mg/L as Cl_2)	
B.10		Chloramine (< 4mg/L as Cl_2; <1 mg/L as NH_3-N)	
B.11		Chlorine Dioxide (< 2 mg/L)	

Data and Analysis

All copper coupons, pipe sections and wires were rinsed and dried after completion of the tests, cross-sectioned (pipes and elbows only), and the exposed surfaces were visually examined and photographed for damage and any rust layers formed. Thickness losses were measured using a Digital Point Micrometer (Mitutoyo Series 342). For weight loss calculations, specimens were weighed both prior to experimentation and after being cleaned using deionized water and Brasso polish to remove rust buildup post-test. Corrosion rates were estimated using a) total weight loss, b) release rate of copper in water (using ICP-MS) and c) maximum thickness loss of each sample. Selected samples from pipe-loop experiments were visually inspected and photographed under a digital microscope (Model zORB; Carson Optical Inc., Ronkonkoma NY) at 50-55X and an Environmental Scanning Electron Microscope (or ESEM; Model FEI Quanta 600 FEG) at 5000X magnifications.

RESULTS AND DISCUSSION

Experiment #1: Long Term Bench Scale Jet Impingement in Hot Water Recirculation Experiments

Effects of pH and temperature (Phase-I)

Copper release rates in soft water conditions (70 °C and 48 °C) were higher than that for corresponding hard waters throughout the experiment (Figure 2-13), irrespective of the pH. There was negligible copper release to hard water conditions before pH was brought down to 7.0. The reduction in pH caused an acceleration of copper release rates in both soft and hard waters (Figures 2-12 and 2-13). Overall, the cumulative copper release was 16X and 4.3X higher in the soft water than hard water, at 70 °C and 48 °C, respectively. However, after 48 days and at extremely high velocity (25 ft/s or 5-15X of recommended), there was no indication of significant erosion corrosion or wall thickness loss. The copper release trend seems consistent with the idea that soft water is more aggressive than hard water at higher temperature (70 °C).

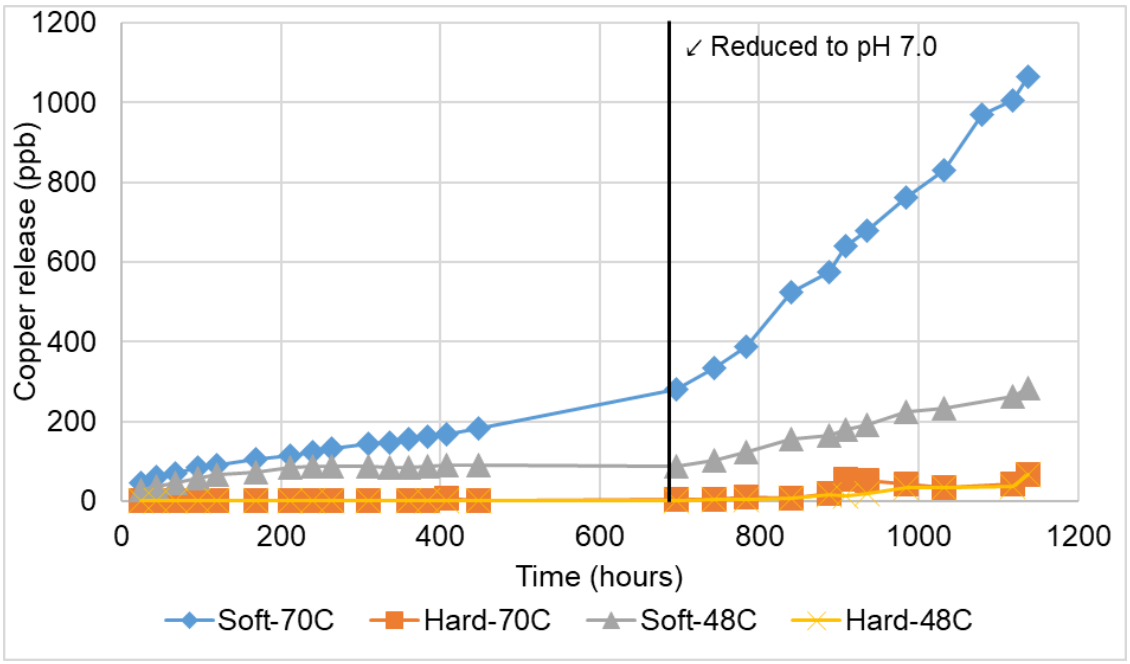


Figure 2-12. Copper release rates for four conditions of 'Phase-I' experimentation (Building X Hard and Soft Waters at 70 °C and 48 °C) at 25 ft/s.

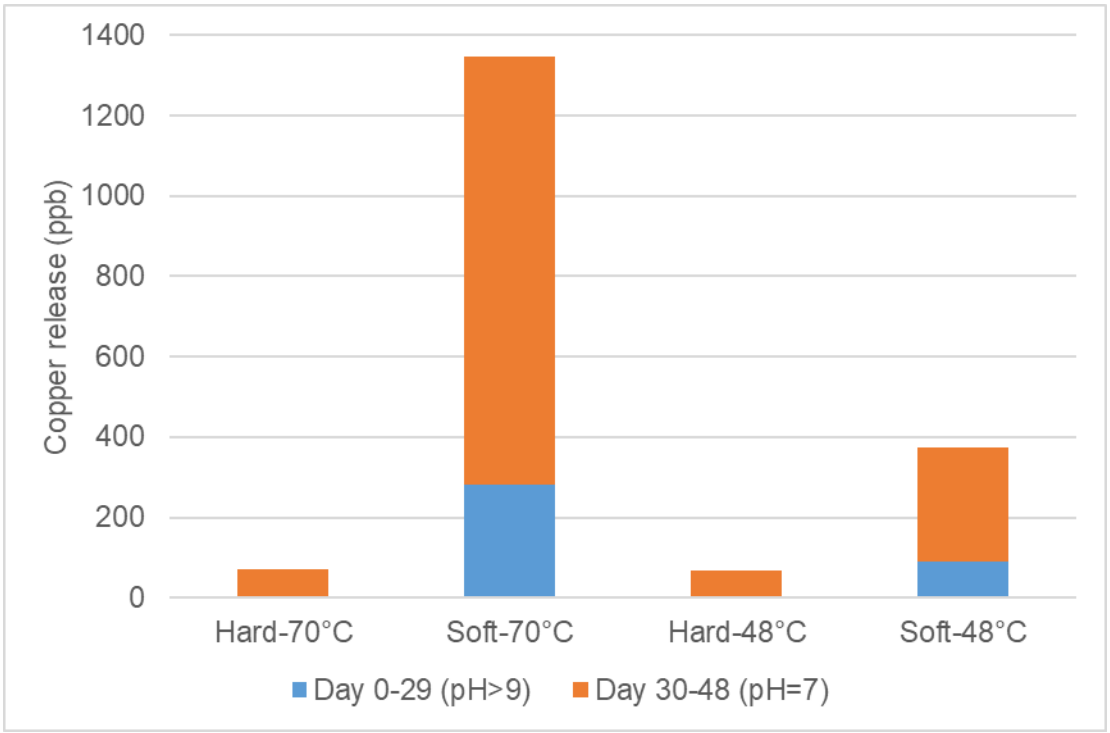


Figure 2-13. Total Copper release for four conditions of 'Phase-I' experimentation (Building X Hard and Soft Waters at 70 °C and 48 °C) over 48 days.

Effect of Water Hardness and Natural Organic Matter (Phase-II)

In Phase-II, natural organic matter (1-2 mg/L) was included and Phase-I tests were repeated with and without NOM (Table 2-3). Prior studies with NOM demonstrated copper corrosion rates 8 times higher than that without NOM (Kristiansen 1977) and that NOM may complex copper to increase release in lower pH water (Edwards, Ferguson and Reiber, 1994; Edwards, Meyers and Schock, 1996; Broo et al., 1998). It was, therefore, hypothesized that this mechanism might also worsen erosion corrosion rates. However, no appreciable thickness losses were seen in any of the eight conditions for over two months.

Relying on Building X's water chemistry (Table 2-2), nitrate and ammonia ions were added on Day 65. El-Egamy noted that copper can corrode faster in nitrate-containing solutions and that the chemical/electrochemical nature of the process would depend on the concentration of nitrate ion and how acidic the medium is (2004). Also, according to Francis (1985), trace amounts of ammonia can also produce abnormal corrosion of copper-nickel alloys.

Within two weeks (Day 79), the copper coupon in the Hard-NOM-65°C condition showed visual signs of concentric erosion corrosion patterns. It could not be established if nitrate caused the non-uniformities to develop or whether they would have naturally occurred. After 107 and 204 days of continuous run time at 25 ft/s (Figure 2-14), the wall thinning rate slowed down for Hard-NOM-65°C condition whereas it stayed high or even increased for the Soft-NOM-65°C and Hard-NOM-48°C waters. The progression of erosion corrosion on the exposed copper pipe surface of the Hard-NOM-65°C condition over 204 days is shown in Figure 2-15 for illustrative purposes. Synergistic effects of NOM with ammonia and/or nitrate might have occurred, and overall the most rapid wall thinning occurred for the hard water NOM condition at 65 °C. But the characteristic patterns of the rapid field failure were not observed and the overall rate of attack is relatively slow especially considering the extremely high velocities of water tested (25 ft/s) compared to the 8 ft/s present in the field. In summary, long-term testing at very high velocities (25 ft/s) using synthesized soft and hard Building X water, revealed that the hard water was much more aggressive in causing erosion corrosion than soft water, based on water chemistries representative of real systems like Building X.

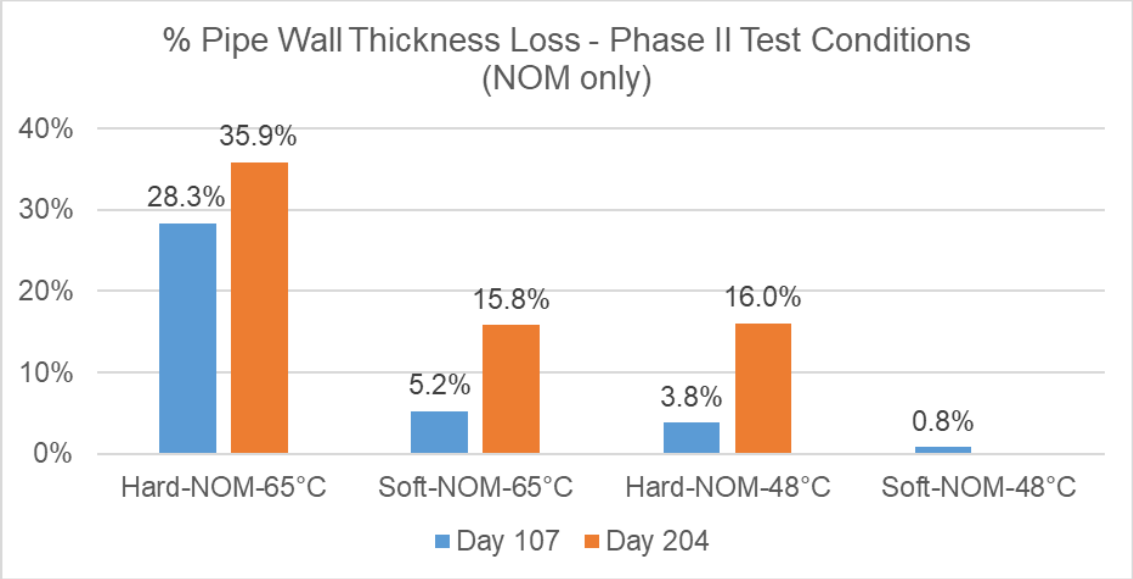


Figure 2-14. Thickness losses in Type M 5/8" copper coupons with NOM (and Ammonia + Nitrate added 66 days after experiment started).

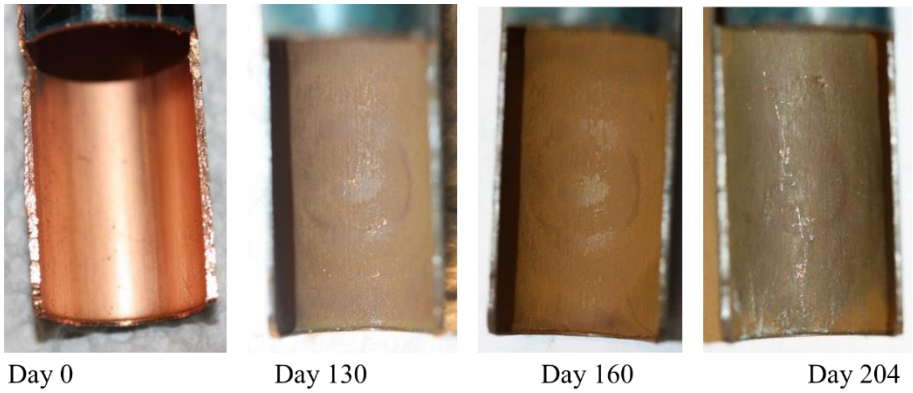
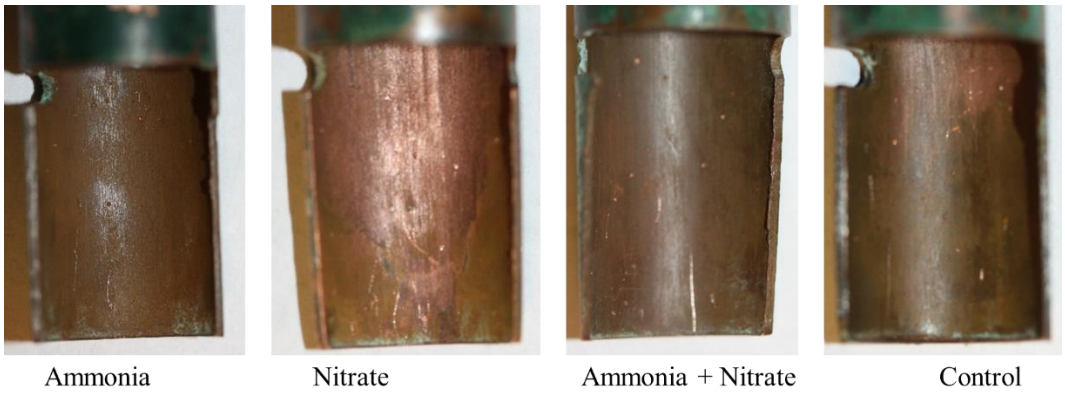


Figure 2-15. Progression of non-uniform erosion corrosion patterns in Hard-NOM-65°C condition (Day 0, Day 130, Day 160, and Day 204). Circular erosion corrosion patterns appeared about 2 weeks after addition of Ammonia + Nitrate (~ Day 79)

Effects of Ammonia and Nitrate (Phase-III)

Out of the four conditions (Only Ammonia, Only Nitrate, Ammonia and Nitrate, None), the Nitrate condition caused the greatest wall thickness loss of 22.4% in 85 days and was visually very distinct from the rest of the copper coupons tested (Figure 2-16), suggesting that this condition had rapid attack. High levels of Nitrate are a characteristic of Building X water and this seems to be the case here as well (Table 2-1). But bubbles were also observed in the water impinged on the copper in this condition due to a design flaw possibly due to incomplete tightening between two CPVC connector fittings, so it is unclear whether the bubbles were the cause or if it was synergistic corrosion for the Nitrate condition. Overall, wall thinning of 16% or more observed in all tests (except the Control) after 85 days, were in the range of that observed at Day 107 in the prior

experiment with NOM. The synergistic effect of NOM with nitrate and/or ammonia, however, may also be important. The characteristic pattern of erosion corrosion seen in field failures was not observed in any condition and the rate of attack was deemed too slow relative to the field failure, considering the extremely high velocity tested.



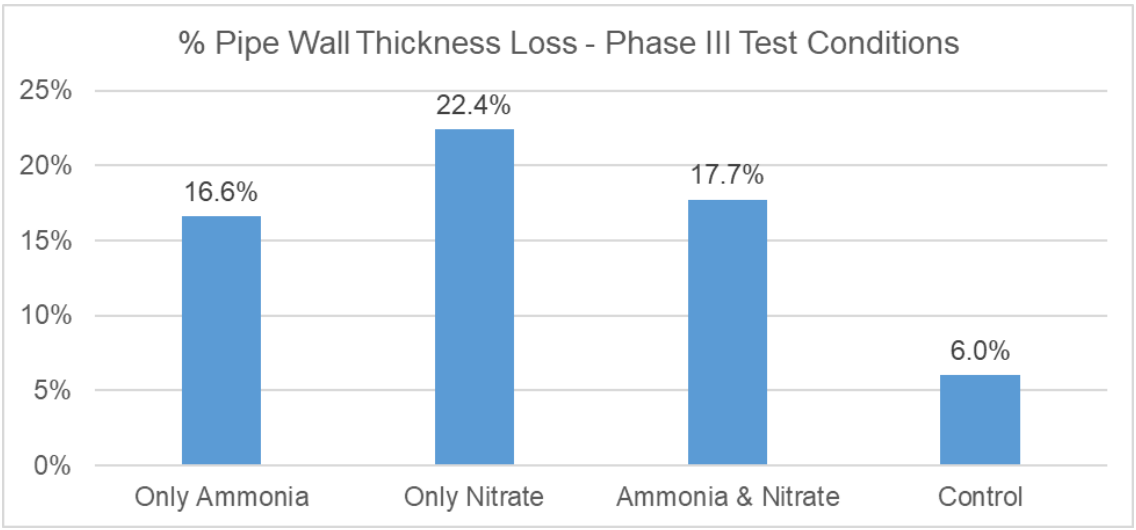


Figure 2-16. (above) Wall thinning of copper specimens after 85 days in pH 7, NOM, and 25 ft/s Building X water with specific additives and (below) respective % Wall thickness loss.

Experiment #2: Large Scale Pipe-loop Hot Water Recirculation Experiments

Severe erosion corrosion damage (including 100% thickness loss or leak) occurred in pipe-loops carrying water with suspended particulates, although the nature and extent of corrosion (type of rust, corrosion patterns, and wall penetration) varied. Corrosion was usually observed in downstream regions just after the elbows in each test loop, where conceptually flowing particles impinged and abraded the wall most severely, especially at 'Elbow #2' (the top bend where water changed directions to a downward direction, Figure 2-10) was typically the first to fail. In the following sub-sections, only 'Elbow #2' ("elbow") failures are discussed for consistency.

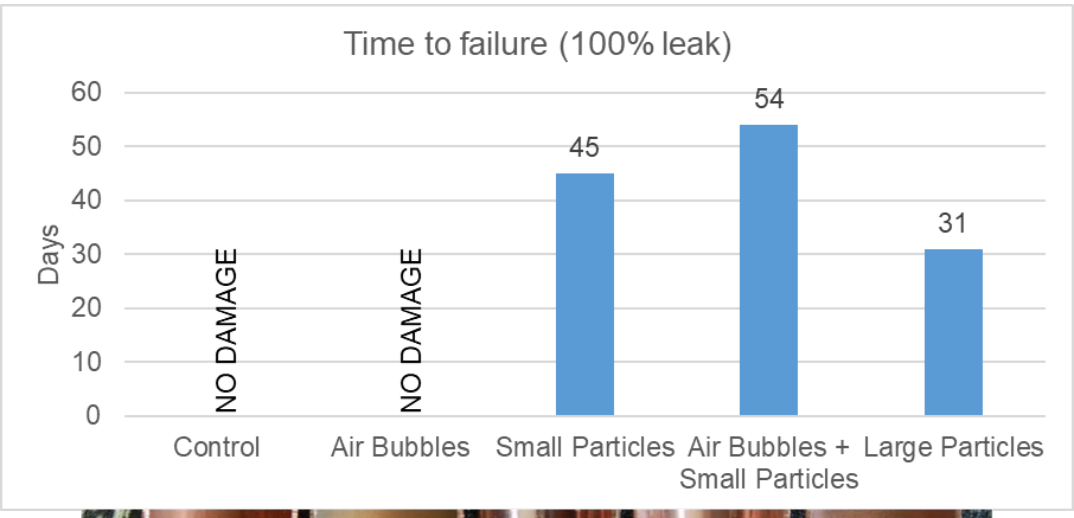
Effects of particulates and particulate sizes

The presence of aragonite particulates caused rapid erosion corrosion damage to copper pipes in all test loops. In the "proof of concept" 'Small Particles' experiment, complete wall penetration occurred at the elbow in 45 days (Figures 2-17 and 2-18). In contrast, the control condition (no particles) saw no thickness loss. For the 'Large Particles' condition, complete penetration of inner copper tube downstream of the elbow was seen in 31 days (Figure 2-18). This is in line with prior research in oil and gas applications, where increase in particle size accelerates erosion corrosion rates. This is likely due to increased and more forceful impacts on the pipe wall at bends. Visually, significant damage occurred all around the pipe diameter. Peppered (or, dent-like) attack markings occurred at both the top and bottom of long straight sections. Oddly, significant corrosion occurred at both the top and bottom of horizontal sections, contrary to expectations In contrast, pipe walls in the 'Small Particles' condition were very shiny and without any corrosion products, as is characteristic in erosion corrosion phenomena. Finally, the elbow for the 'Small Particles + Air Bubbles' system saw 100% thickness loss in 54 days, where the pump often overheated and air locked requiring repeated restarting.

The large particles also destroyed the plastic pump impellers and internal body components very rapidly (Figure 2-19). The impellers failed every 3-4 days and impeller damage, on average, was severe in <36 hours of the pump runtime. Finally, the pump ran at lower velocities after first few hours due to the damage to the plastic impeller.

To our knowledge, this is the first time that erosion corrosion has been reproduced in copper systems carrying potable water of realistic water chemistry and at a reasonably low velocity.

Figure 2-17. (left) Fully penetrating leak in pipe in system with small aragonite particles and (right) close-up of leak



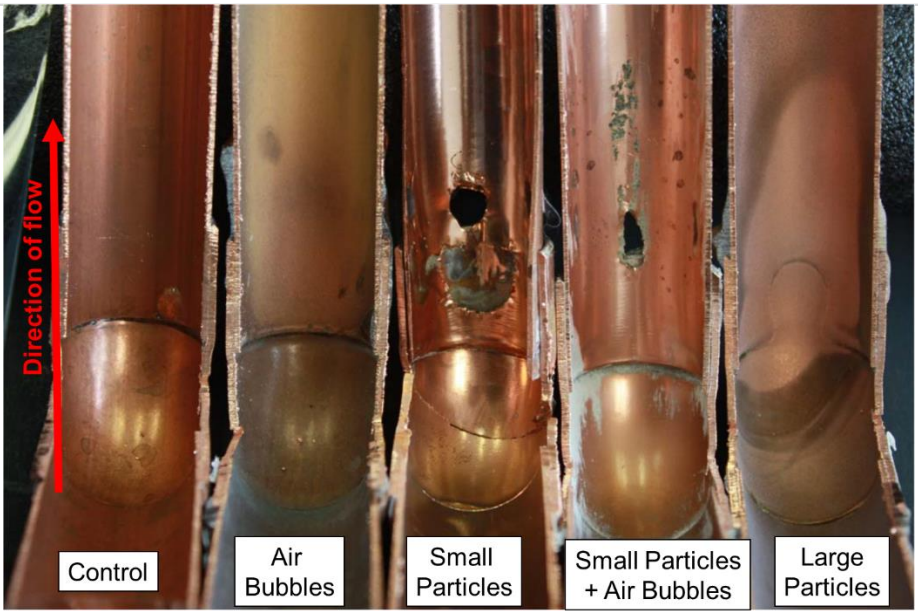


Figure 2-18. (above) Time to failure for 10 ft x 10 ft pipe-loop conditions and (below) close-up photos of elbow damage

Figure 2-19. (left) new impeller compared to damaged impeller in system with large particles, (right) representative hole in plastic pump housing.

In subsequent smaller scale 4 ft x 5 ft pipe-loop tests, pipes carrying small aragonite particles at pH 7.5 and pH 10 failed in a similar and very short time frame (13 days),

whereas the control without did not see any damage (Figure 2-20). While lowering pH typically increases erosion corrosion rates, the rapid mechanistic removal of protective scale and corrosion of underlying metal was very likely dominant mechanism.

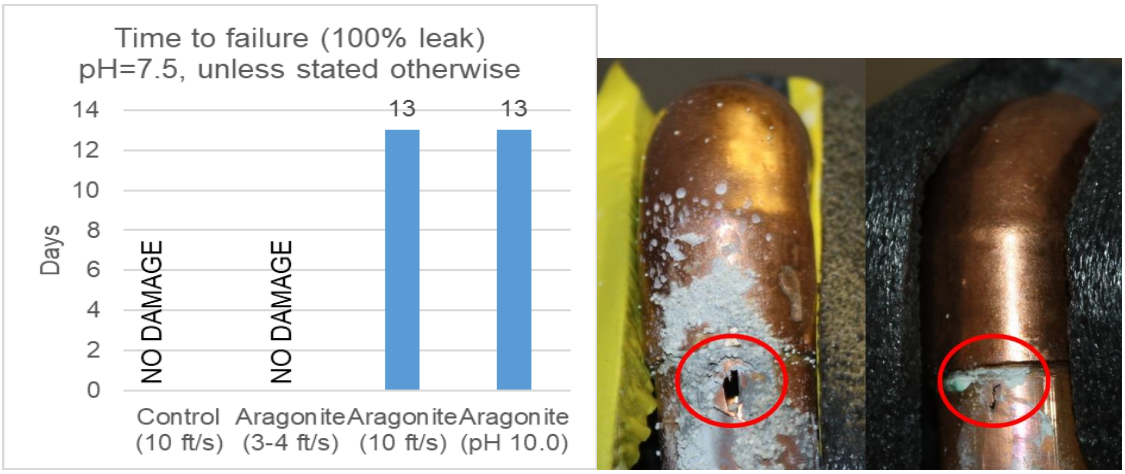


Figure 2-20. (left) Time to failure for 4 ft x 5 ft pipe-loop conditions and (right) close-up photos of elbow damage for aragonite particle conditions and pH 7.5 and pH 10.0

The 'Calcite Particles' condition also witnessed erosion corrosion failures at the elbow in a comparable timeframe of 11-12 days, demonstrating buildup of precipitated and hardened calcite crystals in potable water systems can be harmful to the service life of copper pipes. The extra hardness of aragonite versus calcite (Mohs 4.0 vs. Mohs 3.0) was not as significant to abrasion of copper tube (Mohs hardness 3.0) as was initially believed (Roy et al. 2018).

Effects of pipe-loop geometry (long straight section v/s elbows and horizontal v/s vertical pipe orientation

For the 'Large Particles' condition, thickness losses developed orders of magnitude faster in pipe wall regions immediately following elbows (100%) than in the long straight sections of pipe (10%; seen at 6ft distance on the top wall section of a horizontal pipe) (Figure 2-21). As water flows change direction at bends, the particulates are accelerated centrifugally to the wall of the pipe, leading to impacts focusing on a small surface with an angle of attack causing high abrasion. The flowing test water in pipe-loops witnessed Reynolds Numbers over 50,000, very much in the turbulent zone (>4000). Moreover, the attack occurred all around the pipe diameter, as was evident from comparative visual inspection and ESEM analyses of the pipe wall surfaces of the Control and the 'Large Particles' (Figure 2-22).

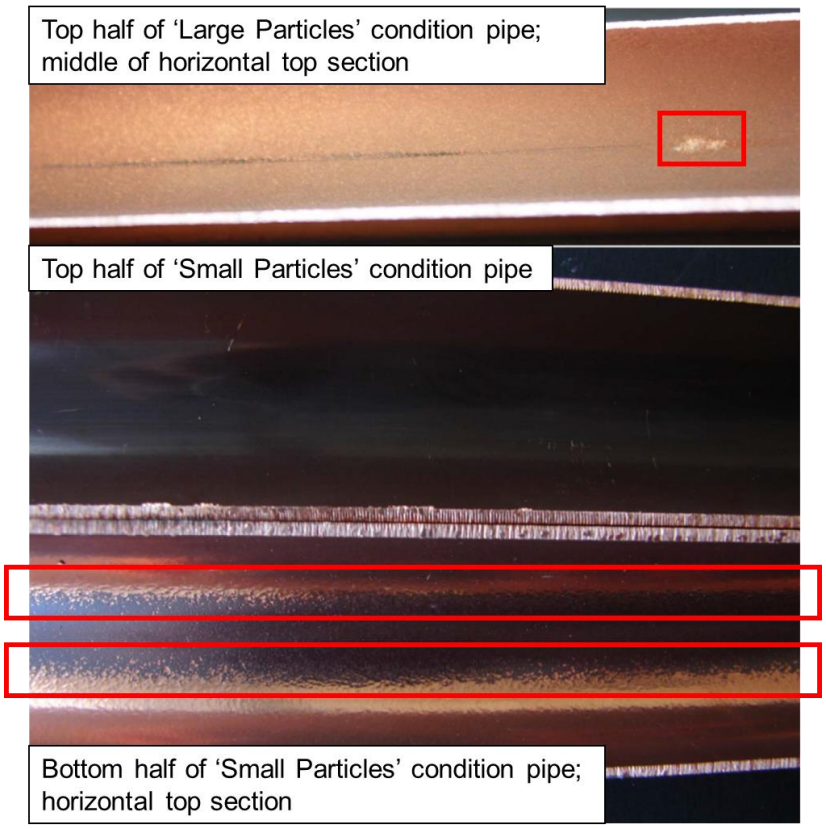


Figure 2-21. (Top) Damage in long straight runs for the 'Large Particles' condition. The featured dent (red box) is on the order of 10% wall thickness loss. (Middle) No such attack seen on the top section of 'Small Particles' condition, (Bottom) Bands of particle damage in small particle test occurs slightly off to the side of the bottom (red boxes).

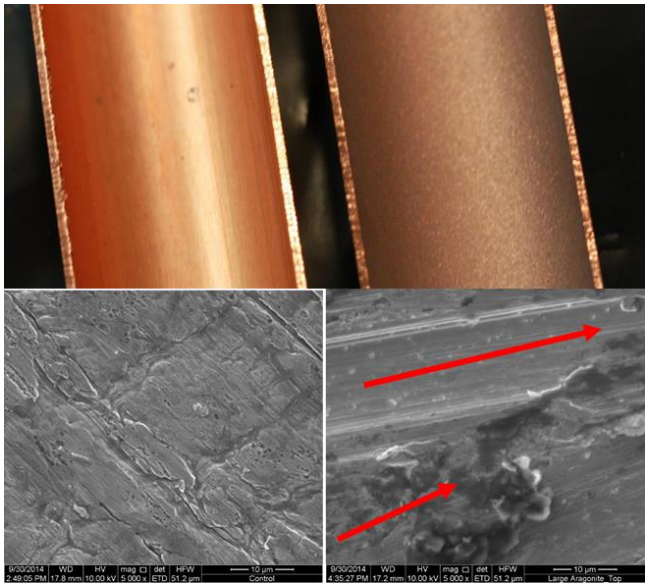


Figure 2-22 (above) Representative photos of top sections of no particles v/s Large Particles (below) ESEM images of their microsurface at 5000X magnification (The red arrows indicate lines of attack in the large particles condition)

Damage in the 'Small Particles' system only occurred on the bottom walls of horizontal pipes and only at some distance from the bends (Figure 2-21). Visual observations via plastic tube sections indicated that the small particles settled to the bottom of the tube, causing significant attack in the middle of the long straight sections (Figure 2-23). The thickness loss along the bottom of horizontal pipes, however, wasn't sizable because the experiment was stopped after the failure of the pipe elbow but these wavy patterns definitely indicated severe denting along the inner pipe surface. No comparable corrosion patterns were seen in the vertical pipe sections, discounting the pipe wall region attacked immediately following elbows.

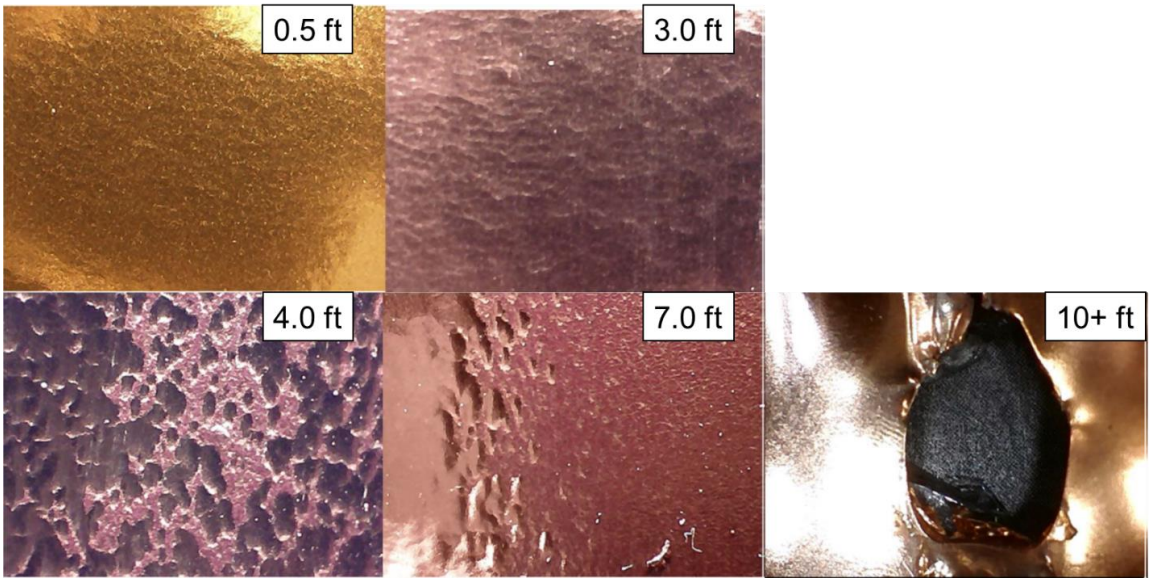


Figure 2-23. Magnified images (53X) along the bottom of the top pipe segment for the 'Small Particles' condition shows damage developed after the bend as particles presumably settled and scoured the pipe wall surface. Label indicates distance from the upstream bend.

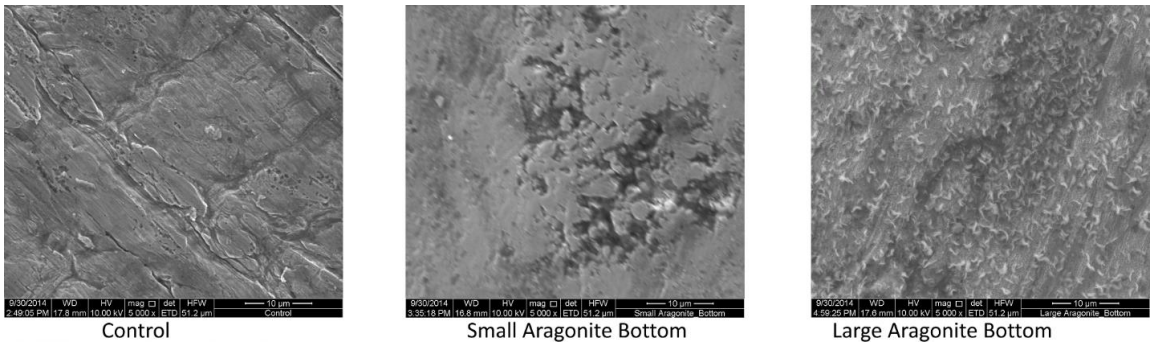


Figure 2-24. ESEM images of the bottom section of horizontal pipes at 5000X mag to compare damage patterns for (left) control, (middle) small particles and (right) large particles.

Effect of air bubbles

The test condition with air bubbles alone did not cause significant erosion corrosion, although it is thought that bubbles can initiate possible abrasion of copper by direct attack or help supply an overabundance of oxygen causing formation of concentration cells (ref).

The Air Bubbles + Small Particles condition witnessed a full leak in 54 days. This is consistent with reporting in the oil and gas industry, that combinations of suspended particles and bubbles, can create synergistic erosion corrosion on pipe walls, which can be far greater than the attack from either particles or bubbles alone. This condition had pump failures 2-3 times/week and pump ran about 2/3rds of the time due to repeated air locking; the total runtime with particle abrasion, was estimate as close to 36 or so days. It is not perfectly clear, but the 36-54 day range, is not much different than the 45 days it took for the 'Small Particles' alone to fail.

Effect of velocity

In contrast to the High Velocity condition of 10 ft/s, the Low Velocity pipe-loop (3-4 ft/s) saw no thickness loss or localized attack patterns after two weeks. Reynolds Numbers for both flow velocities were above 4000 indicating turbulent flow (110000 and 33000-44100; calculated by assuming water density = 1 kg/l, ID of Type M ¾" copper pipe = 0.811", dynamic viscosity of water at 50°C = 0.547 cP). Copper and copper alloys have an associated "critical" or "breakaway" velocity for initiation and propagation of erosion corrosion; for seawater, copper has a breakaway velocity of 2-3 ft/s. However, no such breakaway velocity is available for potable water systems. Current plumbing codes suggest preventative velocities ranging from 1.5 – 8 ft/s (0.46 – 2.4 m/s) for copper, based on scant research (Roy et al. 2018). Finally, velocity profiles get distorted at bends thereby affecting particle impingement velocities and, therefore, bulk water velocities may not be entirely representative of damage at the microsurface level.

Controlling effect of dissolved oxygen

The particle carrying pipe-loops at high velocities (10 ft/s) with rapid failures in a very short time period were exposed to the atmosphere and had dissolved oxygen above 6 mg/L. In contrast, the worst case 'Low Dissolved Oxygen' condition (DO levels decreased to <0.5 mg/L thrice a day) with typical maximum oxygen of 3 mg/L each 8 hours, had only 37% thickness loss at the elbows in the same time that there was a 100% wall thickness loss with saturated oxygen (Figure 2-25). The dramatically reduced rate of attack in the low oxygen condition indicates that corrosion is likely an important contributor to the attack, and that the mechanism is truly erosion corrosion and not just erosion (Figure 2-26). Considering the difference in material hardness of aragonite and copper (Mohs hardness of 4.0 v/s 3.0), erosion by abrasion alone is possible.

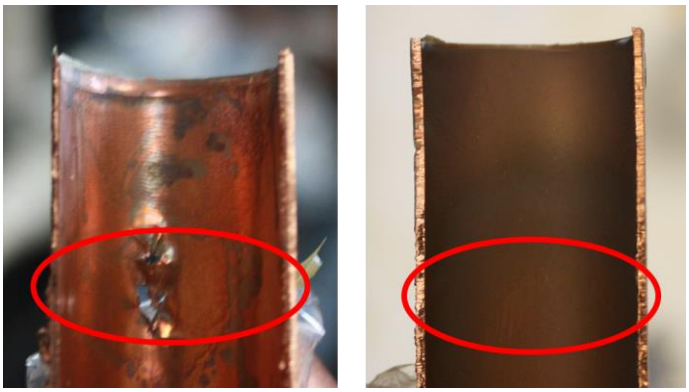


Figure 2-25. Close-up photos of erosion corrosion in (left) ambient dissolved oxygen condition and (right) low dissolved oxygen condition

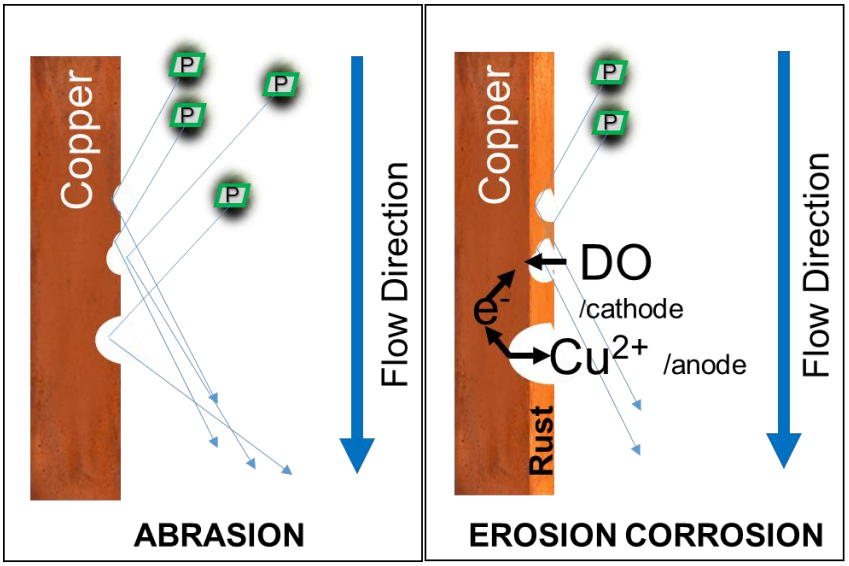


Figure 2-26. (left) Abrasion mechanism strictly dependent on aragonite particles attacking metal and rust layer, (right) erosion corrosion mechanism where particle impingement mechanistically removes metal/scale and electrochemical reactions (corrosion) of underlying metal occurs. DO = Dissolved Oxygen

Experiment #3: Bench Scale Beaker Tests

Effects of particles and particle Size.

Consistent with results from experiments, the presence of particulates accelerates erosion corrosion, and this effect was reliably reproduced in the beaker tests conducted using both calcite and small aragonite particles at 48 °C and 60 °C versus a no particle control condition at 60°C (Figure 2-27). The condition with particles had 7-17X more weight loss than the control. Visually, the attack on copper wires was severe and distributed along parts exposed to the moving particles (Figure 2-28). This strongly suggests that the presence of aragonite (and even calcite) crystals can cause damage to copper tube even at relatively low velocities. Subsequent tests with Medium Particles showed a ~30X

increase in weight loss compared to the Small Particles condition (Figure 2-29). Visually, increase in particle size from no particle condition to small (2 mm) to medium (4.5 mm) leads to more thorough attack on available copper area (Figure 2-30). The Large Particles test witnessed, on average, lower weight loss (with high variability) than Medium (Figure 2-29). Comparing the medium and large particle wires, it appears that the latter was attacked over much less height from the base of the beaker (Figure 2-30). This can possibly be attributed to the decrease in mobility of the heavier particles due to their weight for the designated test velocity (1 gm solid contains ~60 medium particles and ~6 large particles). Additionally, larger particles can imply lesser frequency of attack owing to their relatively large bulk volumes that solo particles have to circumvent before reaching the exposed wire.

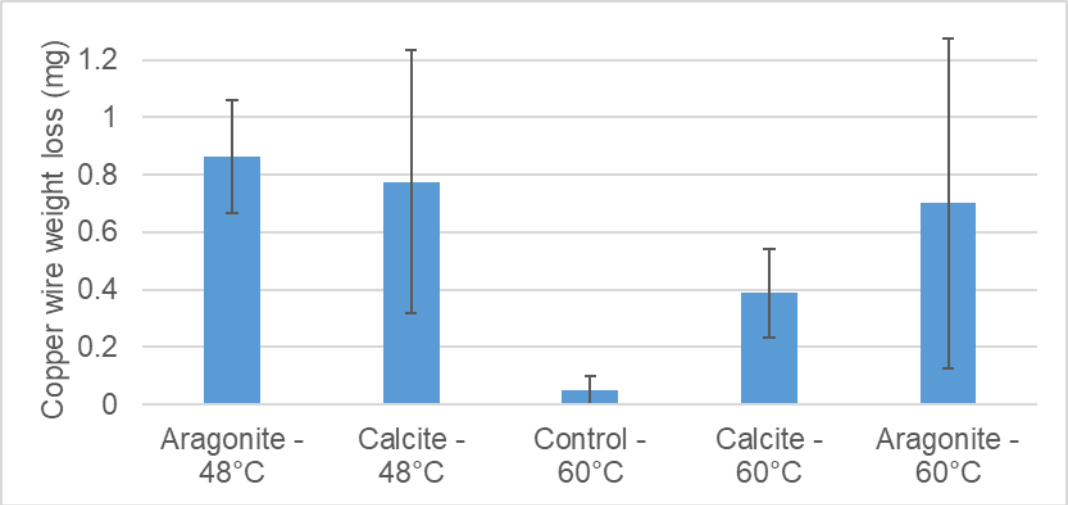


Figure 2-27. Weight loss of copper wires in beaker tests for aragonite and calcite particles at 48 °C and 60 °C (n=4, except control where n=6). Error bars indicate standard error.

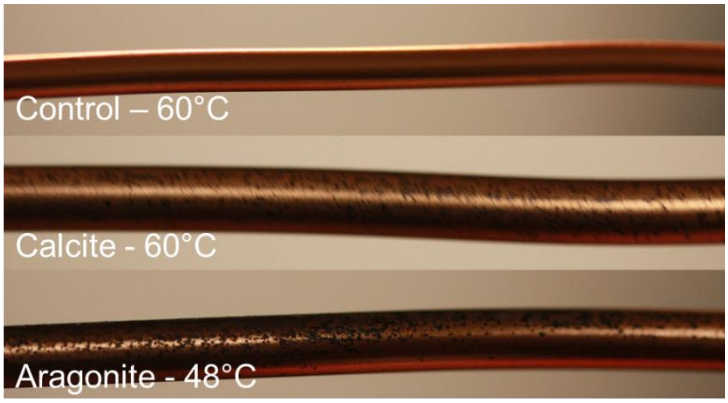


Figure 2-28. Close-up photos of copper wires showing worst erosion corrosion attack for control, calcite and aragonite particles

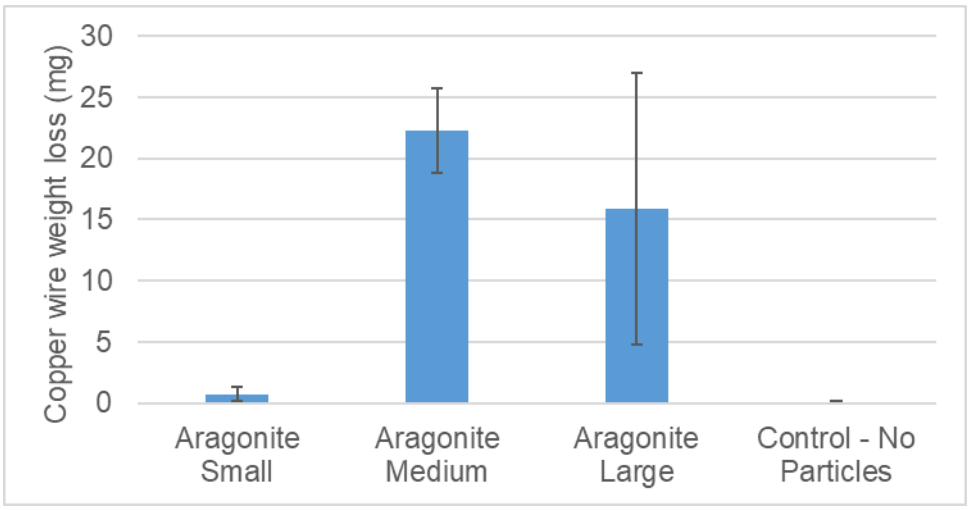


Figure 2-29. Weight loss of copper wires in beaker tests with different particle sizes (n=6) Error bars indicate 95% Confidence Interval.

Figure 2-30. Close-up photos of copper wires showing worst erosion corrosion attack w.r.t. increase in particle size

Effect of disinfectants

The average weight losses for the Chlorine, Chloramine and Chlorine Dioxide and Control are shown in Figure 2-31. The weight loss in the Chlorine condition was significantly higher than other disinfectants (21X w.r.t. the no disinfectant condition) and visually saw severe damage consistent with other research verifying chlorine's aggressiveness in attacking copper metal (Figure 2-32).

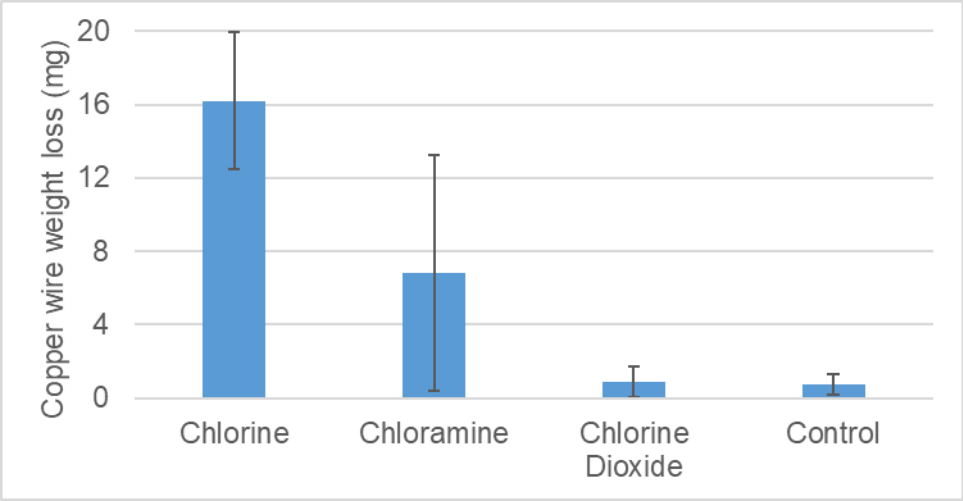


Figure 2-31. Weight loss of copper wires in beaker tests w.r.t. different disinfectants (n=6). The error bars indicate 95% confidence interval.

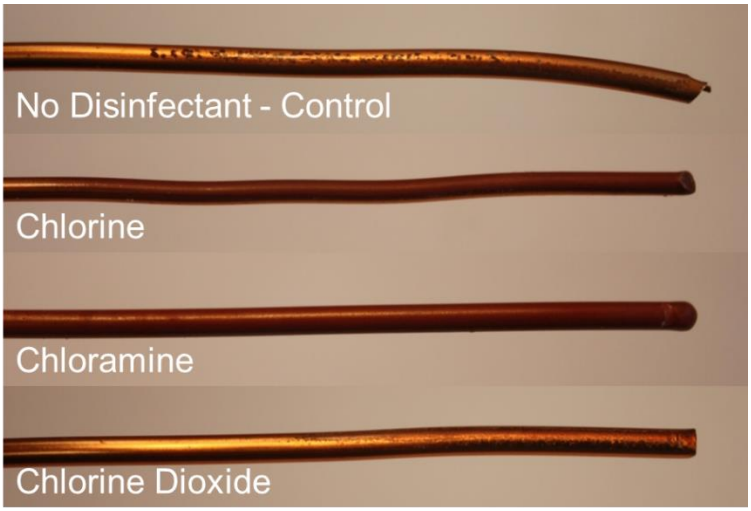


Figure 2-32. Close-up photos of copper wires showing worst erosion corrosion attack w.r.t. various disinfectants

Comparing Corrosion Rates between pipe-loop and beaker experiments

Corrosion rates (in mm/y) were calculated using maximum thickness loss for the pipe-loop and average weight loss for beaker tests respectively. Because the pipe-loops lost more material than just at the leak sites, the calculated corrosion rates are significantly higher than actual rates. Therefore, an exact comparison between both experiments will not be possible. However, the rates are broadly consistent in proving the role of particles in exacerbating erosion corrosion in copper. Corrosion rates for certain test conditions (aragonite particles, pH 7.5, and temperature range 50 °C - 60 °C only) are listed in Table 2-8.

Table 2-8. Corrosion rates of experiments with suspended aragonite particulates at pH 7.5 and water temperature range of 50°C-60°C

Experiment	Test Condition	Water velocity (ft/s)	Corrosion rate (mm/y)	Proportionality Constant k (s/mm)
Pipe Loop (10 ft x 10 ft)	Small Particles	8.5	6.59	3.11×10^{-14}
Pipe Loop (10 ft x 10 ft)	Large Particles	8.5	9.57	4.52×10^{-14}
Pipe Loop (4 ft x 5 ft)	Small Particles	10	22.82	7.78×10^{-14}
Beaker Tests	Small Particles	2.5	0.02	0.12×10^{-14}
Beaker Tests	Medium Particles	2.5	0.65	3.55×10^{-14}
Beaker Tests	Large Particles	2.5	0.46	2.53×10^{-14}

For beaker tests, corr rates in mm/y = 87.6 x Weight Loss in mg / (Copper Density in gm/cm^3 x Exposed Surface Area in cm^2 x Exposure time in hours). Exposed surface area assumed to $5/6^{th}$ of total surface area of copper wires.

The literature suggests material loss rates are usually proportional to the square of the water velocity; cube in the presence of particles (Heitz et al. 1991). At lower velocities, erosion corrosion rates are lower. This exponent further increases as the wall thinning accelerates. Assuming that the velocity squared relationship is true (and no other dependencies for simplicity), the correlation can be shown as follows:

$$\text{Corrosion rate} = k \cdot v^2, \text{ where } v = \text{bulk water velocity, } k = \text{constant}$$

The constant k values determined from the relationship above are listed in Table 2-8. Even for the same particle type (small), no direct comparisons can be made. More representative testing of the same kind (e.g., beaker tests) at different velocities or better estimation of material loss in pipe-loop experiments can help in getting more accurate correlations for formulating erosion corrosion rate prediction equations.

Study Limitations

The particle concentrations studied in the pipe-loop experiments are much higher than will be encountered in real world recirculation systems; however, the underlying water chemistry is very much representative of public water systems with hard water and typically reliant on groundwater.

CONCLUSIONS

This is the first study to reliably reproduce copper erosion corrosion phenomena with realistic freshwater chemistry in laboratory experiments. The following conclusions can be drawn from this study:

- Hard waters without suspended particulates, were equally, if not more aggressive, than soft waters in causing erosion corrosion

- Long term testing for potable water at 5-15X velocities (25 ft/s) and at recommended and higher temperatures alone did not reproduce rapid field failures
- Presence of nitrate anions and natural organic matter may increase erosion corrosion in simulated water of high hardness
- Particles, especially precipitating calcium carbonate hardness as aragonite or calcite, can be a key factor in causing rapid erosion corrosion.
- For potable water with suspended particulates, velocity is a critical parameter in determining effect of particles on pipe walls
- Size of particulates affects the pattern and rate of damage. In general, an increase in particle size, leads to increased attack when particles of equal mass are used.
- Failures are more pronounced in high turbulence areas, like bends, but long straight sections of copper tube can see attack despite operating conditions and water chemistry consistent with plumbing codes
- Qualitatively, lowering pH, increasing flow velocity, increasing water temperatures, entrainment of particles (of bigger sizes), and addition of chlorine disinfectant, increased the rate of erosion corrosion

As an aside, this study also describes a semi-standardized pipe-loop test and a worst case water chemistry that can be used to examine erosion corrosion resistance of other metals and alloys used in drinking water operations. While the pipe-loop method needs refinement, it comes close to simulating real world scenarios in the lab, which provides an important complementary dataset to small scale electrochemical and other testing methods.

Ultimately, copper pipes for potable water systems built within current plumbing codes, are not immune to erosion corrosion if entrained particles are present. With new ASHRAE recommendations (i.e., adoption of hot water recirculation, hotter water temperatures and increased chlorine dosing) to control Legionella, the likelihood of erosion corrosion will only increase putting buildings at increased risk of plumbing damage.

Future work

Future research should examine the effects of lower, more realistic, particle concentrations and how they affect corrosion rates. The effects of adding trace sequestering agents such as polyphosphate in possibly preventing formation of solids and also hindering aging from soft calcium carbonate to harder crystals such as aragonite by the process of crystal poisoning (Stumm and Morgan, 1996) is another relevant focus area. As is use of phosphate to reduce corrosion. Finally, a dimensional analysis of relevant variables can also be attempted.

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CHAPTER 3. EFFECTS OF $CaCO_3$ PRECIPITATION ON EROSION CORROSION OF NONLEADED BRASS IN POTABLE WATER SYSTEMS

Siddhartha Roy and Marc A. Edwards

ABSTRACT

Brasses used in potable water distribution systems had up to 8% lead until January 2014. Thereafter, the 2011 Federal Reduction of Lead in Drinking Water Act came into force to protect the public from lead exposure, requiring new brass alloys that do not exceed a surface-weighted average of 0.25% Pb, and which are termed "nonleaded". Many nonleaded brass products are now available, but their propensity to fail as a result of erosion corrosion is unknown This study tested the performance of commercially available nonleaded brass elbows (C46500) in a recirculating Cross-linked Polyethylene (also called, PEX) rectangular pipe loop by exposing to hard water with high concentrations of suspended aragonite particulates that form at high temperature and conditions on the surface of heating elements. Fully penetrating leaks occurred in the elbows in an alarming 13.5 days at 13 ft/s (4 m/s) and 50-55°C at pH 7.5, whereas an identical condition without particles remained undamaged. Further investigation showed erosion corrosion can be severely accelerated dependent on pH, flow velocity, particle size, and type of disinfectants present. This is the first study to demonstrate that nonleaded brass fittings (C46500) are especially vulnerable to rapid failures due to erosion corrosion.

KEY WORDS: erosion corrosion, nonleaded brass, hard water, calcium carbonate, aragonite

INTRODUCTION

Used as an engineering alloy for over a millennium, brasses (typically copper-zinc alloys with other trace metal elements) are widely used for intricate components in drinking water distribution systems. The plumbing devices with critical brass components include pipes, plumbing fittings, valves, heat exchanger tubes, water meters, backflow preventers, bearings, and pump impellers. These copper alloys are preferred for such applications because of their "good strength and ductility … combined with excellent corrosion resistance and superb machinability."[1] In general, the service life of these components is expected to be at least 20 years, and more commonly 50 to even 100 years performance can be achieved.

Basses used in water distribution operations have traditionally had up to 8% lead (termed "lead free") until early 2014, after which the 2011 Federal Reduction of Lead in Drinking Water Act was in force.[2] The new law mandated that lead levels in brass should not exceed a weighted average of 0.25% (referred to as "nonleaded") of the wetted surface (i.e. the surface that comes in contact with potable water). Manufacturers have responded to this legislation by replacing lead in their alloy products with alternative metals like bismuth, selenium, phosphorus, zinc, tin, and aluminum.[3,4] An additional advantage was that these alloys do not leach harmful metals like lead, and it was hoped that their resistance to corrosion and cavitation would be at least as good as the alloys that contained lead.[5]

Erosion-Corrosion

Erosion-corrosion can be described as the localized wearing away of material due to rapidly flowing corrosive liquid, and typically occurs at relatively high flow rates (velocities) in the presence of dissolved oxygen. Erosion corrosion is exacerbated by high temperature, particulates and air bubbles, and other factors.[6] Brasses typically form protective scales and other corrosion products on their wetted inner surfaces[5] specific to the dissolved gases and chemistry of the water it comes in contact with. These protective layers are critical to lowering corrosive rates of attack to levels that allow brass materials to function for decades or even centuries.

It is thought that severe hydrodynamic conditions, like high water velocity, particles, or cavitation, can remove the protective coating and expose the underlying alloy to excessive rates of corrosion resulting in premature failures. In premise plumbing, very high water velocities and pressure drops are often encountered in bends, tee-sections, valves, and pump impellers, and at these locations brass alloys can be vulnerable to attack. Syrett hypothesized a "breakaway velocity" for initiation of erosion corrosion specific to different copper alloys.[7] Cohen recommends using "erosion-resistant alloys"[8], but long term resistance of the newer nonleaded brasses has never been examined.

Recent testing by the Plastics Pipe Institute concluded that brass fittings are unlikely to experience erosion-related damage[9]. Turkovic and colleagues examined four nonleaded alloys using a short-term erosion corrosion resistance test where the specimens showed

negligible damage.[5,10] However, this testing failed to take into account factors like low pH, very high velocities, presence of particles, etc. that are known to contribute towards rapid failures.

Other studies have also looked at nonleaded brass in drinking water applications and concluded they were "suitable for use" and unlike to cause any "increase in failures",[11-13] except for one paper[14] that described premature failures in nonleaded brass pump impellers used in water distribution systems. These impellers are subject to very high velocities (50-140 ft/s or 15-43 m/s) and, therefore, not representative of premise plumbing operations, but nonetheless the report is cause for concern.

Particles and water hardness precipitation in premise plumbing

Particles are always present in premise plumbing from a variety of sources including source waters, treatment processes, external contamination, corrosion products from the distribution systems, and precipitation of carbonate hardness in water heaters.[15-16] In general, concentrations of particles are low, but there is also a push towards increasing temperatures in hot water recirculation systems from the current 48°C to 60°C[17] to control growth of pathogens like *Legionella pneumophila*. Higher temperatures exacerbate erosion corrosion and accelerate precipitation of water hardness ions in solids such as $CaCO_3$.[18-19]

Calcium carbonate precipitation can occur as either soft or very hard particulates; aragonite is an example of the latter. In fact, aragonite particles precipitated and accumulated in a hot water plumbing system (Figure 3-1) in California made of copper causing widespread erosion corrosion and significant infrastructural degradation in a few years.[20] These suspended particles might contribute towards material degradation by erosion from solids impingement as well as classic erosion corrosion.

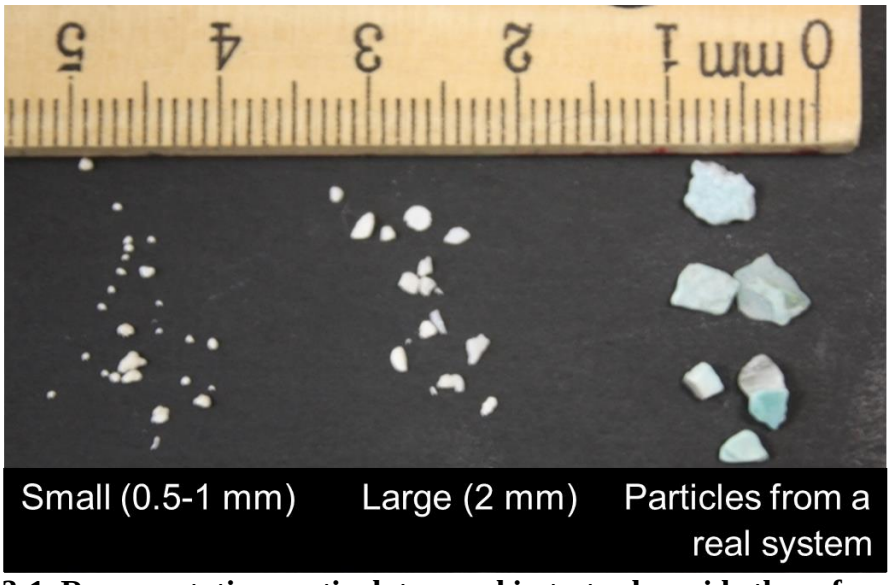

Figure 3-1. Representative particulates used in tests alongside those from a real system

An experimental study by Roy and Edwards showed the potentially disastrous role of suspended particulates in exacerbating attack from erosion corrosion on copper,[19] which has led to a standardized means of rapidly testing erosion corrosion resistance in the laboratory. This approach was extended to nonleaded brass fittings used in potable water systems. Parallel experiments conducted in the absence of oxygen have demonstrated minimal damage to copper, providing that the operative mechanism of attack is erosion corrosion and not abrasion.

Objectives of this study

In this work we examine the role of suspended particulates (presence/absence), pH 7.5 versus 10, velocities of 6 ft/s (1.8 m/s) and 13 ft/s (4 m/s), particle sizes of 0.5-1mm, or 2mm), and type of disinfectants including free chlorine and chloramine.

Lower *pH* waters are more aggressive than higher pH ones for erosion corrosion.[20] The *velocity* (and temperature) of flowing water greatly influences erosion corrosion, but the threshold values at which attack occurs depend on the specific chemistry and circumstance. As a result, there are over 10 velocity threshold recommendations designed to prevent erosion corrosion in copper ranging from 1.5 to 8 ft/s (0.45 to 2.4 m/s),[19] but there are no guidelines for nonleaded brass used in potable water systems. According to some estimates, erosion corrosion rates can be directly proportional to the square or even cube of the bulk velocity in the presence of particles.[21]

The *size of particulates* (along with particle concentration, shape, microstructure, impact angle, etc.) is an important parameter and can influence damage initiation and propagation.[21] The size and type of particles will dictate whether they will remain suspended or settle, as well as the rate and magnitude of erosion corrosion.

Water utilities across North America also often add a *disinfectant* residual (like free chlorine, chloramine, etc.) to deactivate microorganisms before sending the treated water into the distribution system. Free chlorine is a strong oxidant, extremely reactive and known to exacerbate brass corrosion problems such as pitting and dezincification.[22] It is anticipated that chlorine residuals in the water will accelerate erosion corrosion. Chloramines (formed by reacting chlorine and ammonia) can possibly contribute to corrosion owing to released ammonia in the water. Specific testing examining how free chlorine and chloramine can influence (or thwart) brass erosion corrosion has never been carried out, and is worthwhile.

EXPERIMENTAL PROCEDURE

Pipe-Loop Apparatus

Seven conditions were tested (Table 3-1) in pipe-loop apparatuses (Figure 3-1) to test the performance of nonleaded brass (C46500) fittings in premise plumbing systems. The experiments were conducted to study the effects of aragonite particulates (whether

precipitating or otherwise present), particle size, pH, velocity, and type of disinfectant on brass erosion corrosion.

Table 3-1. Summary of experimental conditions in this study

Test Name	Particulates	pH	Velocity (ft/s)	Disinfectant
1 – *No particles*	–	7.5	13 (4 m/s)	–
2 – *Small Particles*	Small	7.5	13	–
3 – *Large Particles or Low pH or High velocity or No Disinfectant*	Large	7.5	13	–
4 – *High pH*	Large	10.0	13	–
5 – *Low velocity*	Large	7.5	6 (1.8 m/s)	–
6 – *Chlorine*	Large	7.5	13	Free Chlorine (up to 4 mg/L)
7 – *Chloramine*	Large	7.5	13	Chloramine (up to 4 mg/L)

Recirculating pipe-loops were constructed (Figure 3-2) with ½ in crosslinked polyethylene (or PEX) pipe, and joined using ½ in dezincification resistant naval brass (UNS C46500) elbows purchased from a commercial retailer. The pipe loop dimensions were 4ft x 5ft or 1.21 m x 1.52 m (vertical x horizontal) with test water (see Table 3-2 for chemistry) stored in 5 gallon polypropylene reservoirs, and circulated using submersible pumps (Superior Pumps Model 91250 ¼ HP). The approximate surface composition of the brass elbows (by weight) was determined using an X-ray fluorescence (XRF) device (Innov-X Systems, Model Alpha 8000) to be: 60.9% Cu, 38% Zn, 0.2% Pb, 0.8% Sn, and 0.1% Fe.

For the *'Low velocity'* test, the velocity was reduced from the pump default of 13 ft/s (4 m/s) to 6 ft/s (1.8 m/s) by diverting part of the flow back into the reservoir using a PVC tee-section.

Water Chemistry and Test Conditions

A test water with high hardness and high alkalinity (Table 3-2) known to cause serious copper erosion corrosion was used.[20] The test water was synthesized prior to water changes every week using deionized water and reagent grade sodium, calcium and magnesium salts. The pH of test waters was adjusted twice a day using CO_2 gas and NaOH stock solutions, and measured using a double-junction Ag-AgCl electrode (Fisher Scientific).

Water temperatures stayed in the range of 50-55°C, which is typical of hot water recirculation systems, due to the heat naturally generated by the pumps and mechanical energy input to the system.

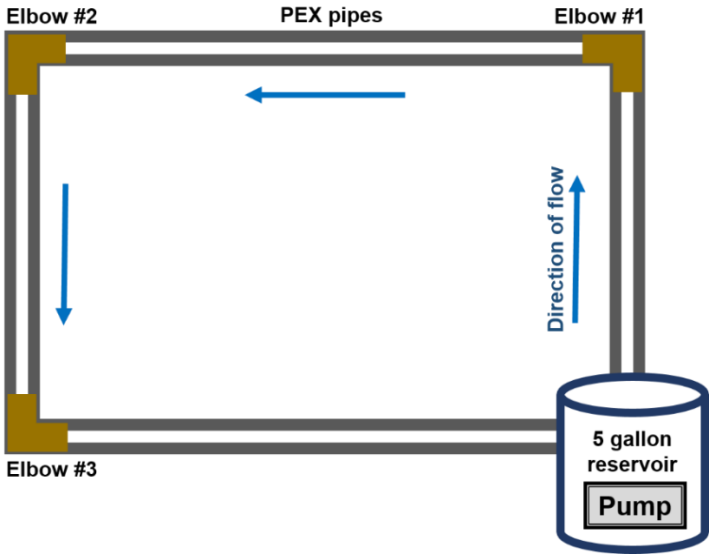

Figure 3-2. Schematic of pipe-loop apparatus for erosion corrosion testing of nonleaded brass

Table 3-2. Chemistry of the test water for erosion corrosion experimentation

Parameter	Unit	Target Value
Total alkalinity	mg/L as $CaCO_3$	290
Hardness	mg/L as $CaCO_3$	390
Calcium	mg/L	85
Magnesium	mg/L	44
Sodium	mg/L	37
Chloride	mg/L	49
Nitrate	mg/L (NO_3-N)	25
Sulfate	mg/L	66
Natural Organic Matter (NOM)	mg/L	1-2

Disinfectant residuals were manually adjusted in 'Chlorine' and 'Chloramine' tests twice a day. Chlorine was dosed as sodium hypochlorite from concentrated bleach (NaOCl solution stock) to achieve a 4 mg/L residual concentration (as Cl_2). Chloramine was formed by dosing sodium hypochlorite and ammonium hydroxide to achieve 4 mg/L of total chlorine (as Cl_2) and 1 mg/L of ammonia (as NH_3-N). Free chlorine and total chlorine (for 'Chloramine') residuals were measured using a DPD (diethyl phenylene diamine) colorimetric test on a Hach(†) Portable Spectrophotometer DR2700 as per Standard Method 4500-Cl G.[23] Ammonia was measured on the spectrophotometer using the Salicylate method as per Standard Method 8155.[24]

Data and Analysis

All brass elbows were rinsed and dried after completion of the tests, cross-sectioned, and the inside surfaces were visually examined for damage and any rust layers formed. Thickness losses of the brass walls were measured using a Digital Point Micrometer (Mitutoyo Series 342). Selected samples from experiments *'Control', 'No Particles',*

'Large Particles', 'Low velocity', 'Chlorine' and *'Chloramine'* were visually inspected and photographed under an Environmental Scanning Electron Microscope (or ESEM; Model FEI Quanta 600 FEG(†)) at 100x and 200x magnifications.

RESULTS

Erosion corrosion damage occurred in all brass specimens exposed in test loops with suspended particulates, although the nature and extent of damage (type of rust, corrosion patterns, and wall penetration) varied. Corrosion was observed in all three elbows illustrated in Figure 3-1 within each pipe loop. However, only results for 'Elbow #2', and specifically the downstream end, are discussed here for consistency, because it was the first to fail.

Effect of particulates

Holding all other variables constant, the *'Large Particles'* test caused 100% wall penetration in about 324 hours (or 13.5 days) whereas the *'Control'* (with no particles) had no significant damage (Figure 3-3[a]). Similar erosion corrosion rates were also observed by the authors while testing copper plumbing systems, where 'Elbow 2' bends also were first to fail.[19]

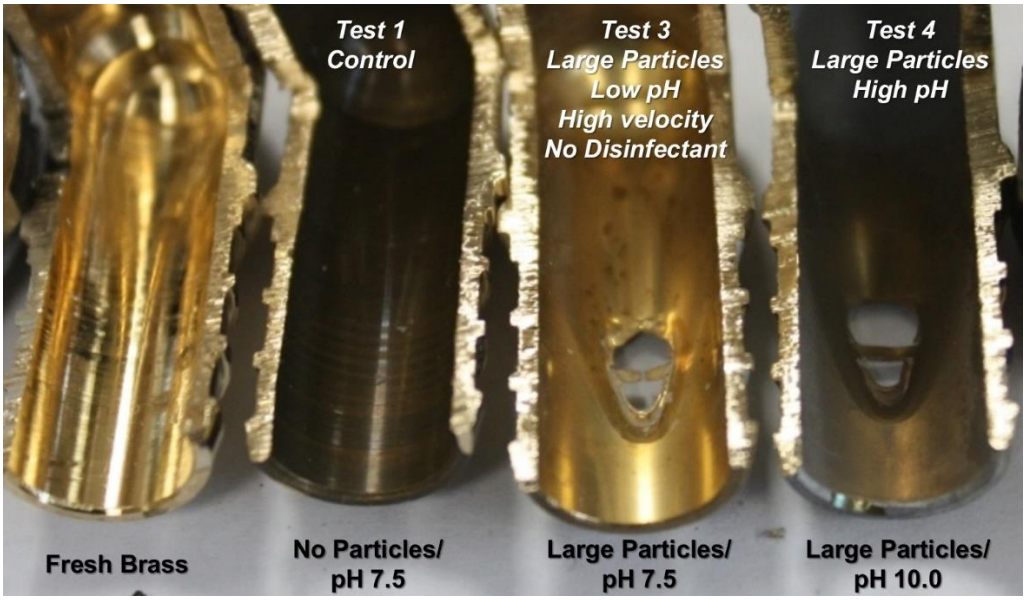

Figure 3-3[a]. Side-by-side comparison (L-R) of fresh brass with tested conditions of 'Control' and 'Large particles' at pH 7.5 & 10

The surface characteristics of the *'Control'* specimen indicate formation of a black protective oxide film, readily occurs in this hot water without particulates as hypothesized,[25] but it did not occur with the suspended particulates. The specimen surface of *'Large Particles'* condition, on the other hand, was shiny and devoid of any such film, with deep grooves and wavy patterns which are consistent with previous descriptions of erosion corrosion in the literature[26] and field samples.

While *Control* did not witness any thickness loss, ESEM analyses (Figure 3-3[b]) indicate shallow channels in parallel on parts of the surface, which could be a result of manufacturing than being induced by impingement of high velocity water. The *'Large particles'* specimen (Figure 3-3[b], right) clearly shows wavelet or horseshoe shaped attack at 100x magnification, and is also revisited in the following sections as a point of comparison.

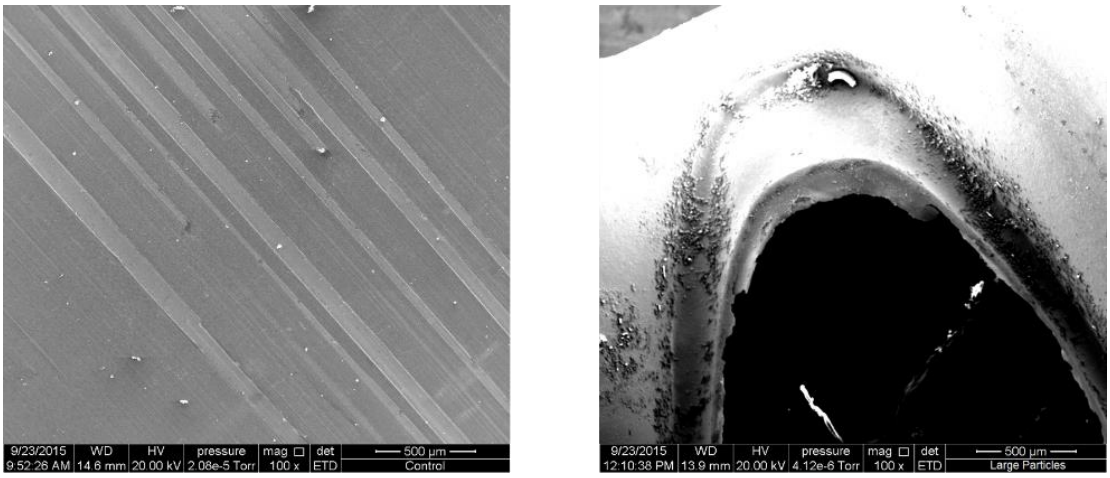

Figure 3-3[b]. ESEM images of no particles (L) and large particles (R) conditions both at pH 7.5 (100x magnification)

While it is acknowledged that many plumbing systems will not encounter the very high particle concentration levels used in our experiments, particles, in general, are almost always present at some level and still pose a threat to piping infrastructure and can initiate failures at relatively low flow velocities.[27-28] This testing method can, therefore, be used for comparing performance across different alloys.

Effect of pH

The *'Large particles'* (or *'Low pH'*) and '*High pH'* tests were carried out at pH 7.5 and 10 respectively at a velocity of 13 ft/s (4 m/s). Both resulted in rapid leaks (Figure 3-3[a]), but the *'Low pH'* condition failed 40% faster than the *'High pH'* condition (Figure 3-4). Lowering the pH typically reduces the likelihood of protective oxide layer formation on the surface of copper alloys[7] and increases dissolution rates, making erosion corrosion more 'conducive'.[29] Knutsson's testing on copper tubes also revealed similar outcomes at even lower velocities and high temperatures.[18]

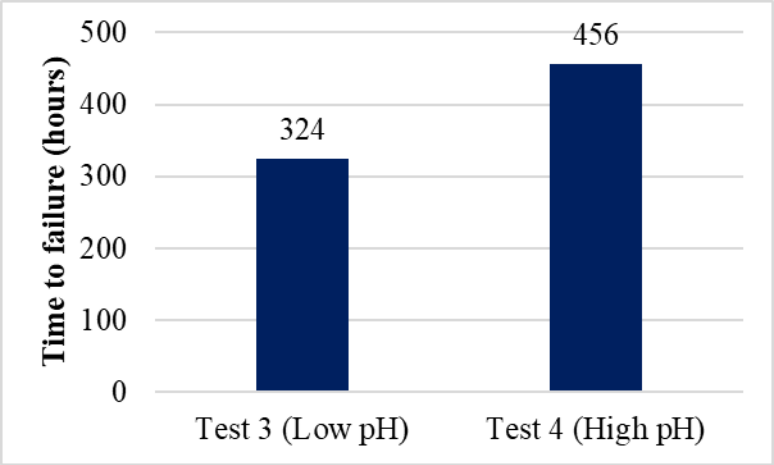

Figure 3-4. Time to failure of brass elbows at pH 7.5 & 10 due to erosion corrosion

Visually, the *'High pH'* brass specimen appears duller (Figure 3-3[a]), despite corrosion patterns being very similar to the low pH condition.

Effect of velocity

'Large particles' (or '*High velocity'*) and *'Low velocity'* tests were carried out at velocities 13 ft/s (4 m/s) and 6 ft/s (1.8 m/s) respectively, both at pH 7.5. As discussed before, the *''High velocity'* test created a full leak in 13.5 days, but the *'Low velocity'* test piece in the same duration and at a little less than half the velocity lost only 5.7% wall thickness (Figure 3-5[a]). This 17X difference in erosion corrosion damage illustrates how high velocities (both localized and in the bulk flow) can be fundamental to erosion corrosion attack.[30-31] However, even the lower velocity would be expected to cause a failure in only about 237 days (if erosion corrosion rates stay constant).

A comparison of Reynolds Number Re (approximate) of both tests (31,000 v/s 14,000) also illustrates the turbulence inside the brass elbows (Re > 10,000 is considered turbulent flow). The horseshoe-like[28] erosion corrosion patterns (i.e. open ends of the pits face downstream of the direction of water flow as if a horse were walking upstream) at the lower velocity (Figure 3-5[b]) creates a shiny reddish appearance, and considerably differ from the clean wavy patterns discussed before in high velocity testing (Figure 3-3[a]). It would appear that identical test waters produced seemingly distinct erosion corrosion damage as a function of velocity. But it is very likely that higher velocities exacerbate severity of the attack to such an extent the characteristic horseshoe shaped pits are not clearly seen because of acute thinning and even failure.[32] The rust layers in the low velocity condition are more pronounced, and need to be further analyzed to evaluate selective leaching of metals and changes in the surface composition owing to erosion corrosion.

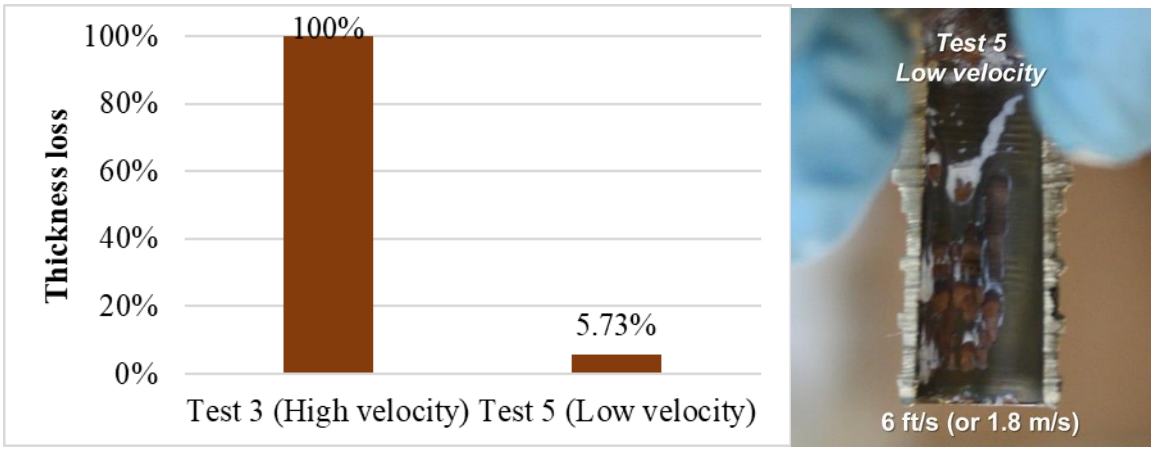

Figure 3-5[a]. (left) Max. thickness loss in nonleaded brass at high and low velocities after 13.5 days; 3-5[b]. (right) Horseshoe-shaped erosion corrosion patterns at low velocity condition

Effect of particle size

The *'Small particles'* and *'Large particles'* experiments utilized small (< 1mm) and large (1-3 mm) aragonite particles respectively at pH 7.5 and a velocity of 13 ft/s (4 m/s). The rate of erosion corrosion for the large particles condition was almost 3X that of the small particles one (Figure 3-6[a]) for the time span of 13.5 days, when the former caused a fully penetrative hole (Figure 3-3[a]). Visually, the wavy patterns formed in the small particles (Figure 3-6[b]) appear very similar to that witnessed in the large particles but the former are more gradual and less pronounced.

While particle concentrations in bulk water were identical for both tests, small particles in flowing water could very well be at higher concentrations because they might have been sucked in by the pump. The larger particles appeared to be sharper (Figure 3-2) and very likely aided attack on brass because the particle surface microstructure (and mechanical hardness) of the particles influence the damage for every impingement.[21,33] High temperatures in water heaters can induce precipitation of carbonate salts; the higher the temperature, the more likely that crystallized particles are bigger in size and have a greater propensity for erosion corrosion.

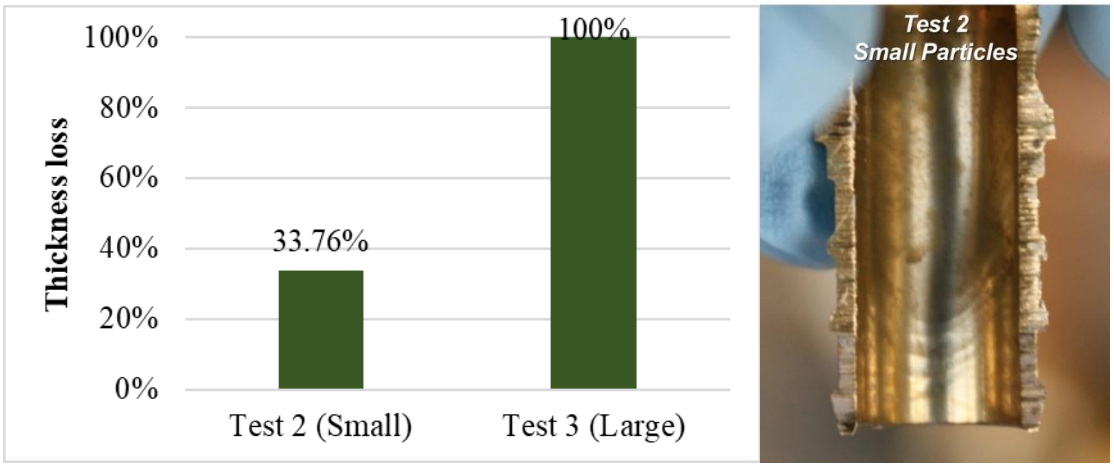

Figure 3-6[a]. (left) Maximum Thickness loss in nonleaded brass witnessed with small & large particles after 13.5 days; 3-6[b]. (right) Erosion corrosion patterns with small particles

Effect of disinfectant type

The *'Large Particles'* (or *No Disinfectant'*), *'Chlorine'* and *'Chloramine'* tests represent conditions with no disinfectant, free chlorine (up to 4 mg/L) and chloramine (up to 4 mg/L) respectively, in a test with with large particles, pH 7.5 and velocity of 13 ft/s (4 m/s). While all three conditions caused accelerated attack and complete wall thickness loss, the brass elbow exposed to free chlorine failed 4.5X faster, while that with chloramine failed ~1.8X faster than the no disinfectant condition (Figure 3-7[a]).

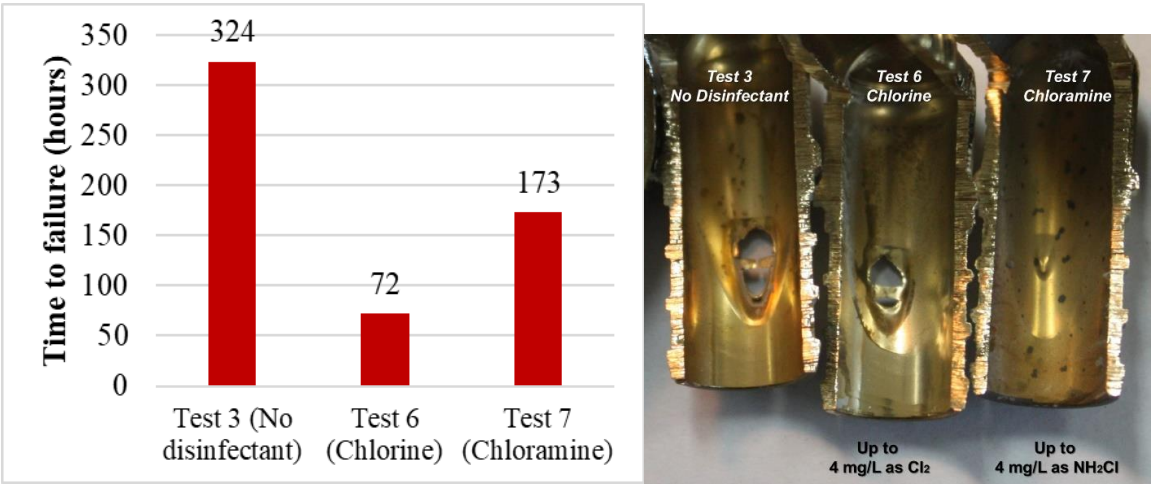

Figure 3-7[a]. (left) Time to failure for nonleaded brass failures without and with disinfectants (chlorine and chloramine); 3-7[b]. (right) Side-by-side comparison of tested brass pieces

Visually, the aggressiveness of chlorine is apparent in the pitted damage along the surface immediately following the bend (Figure 3-7[b]). This is even more noticeable when the surface is enlarged using ESEM imaging (Figure 3-8[b]). Chlorine was taken up very

quickly every time it was dosed, and it is suspected that this was both because of uptake by particles as well as reactions with exposed brass surface causing increased corrosion.

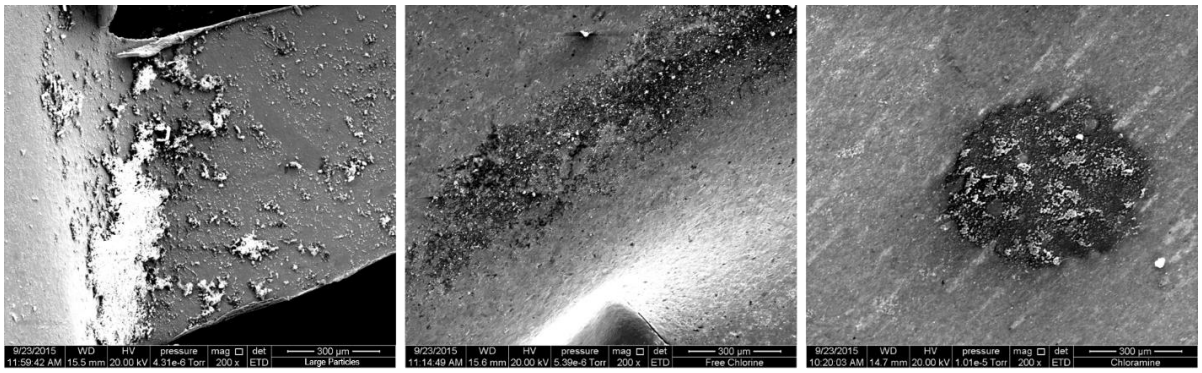

Figure 3-8 [a-c]. ESEM images (200X mag) of tests with no disinfectant, chlorine & chloramine

Damage in the *'Chloramine'* condition appeared relatively less aggressive, and showed distinct dark spots spread across the surface which need to be further analyzed (Figure 3-8[c]). While it is not clear in the image (Figure 3-7[b]), the thickness loss is nearly 100% for chloramine. Material loss is more pronounced in chlorine than chloramine.

CONCLUSIONS

The following are the major conclusions obtained from the study:

1. Nonleaded brass fittings witness accelerated erosion corrosion in the presence of particulates. Surface damage was shiny and devoid of corrosion rusts consistent with descriptions found in the literature.

2. Lowering pH of potable water can increase erosion corrosion rates as has been demonstrated in prior corrosion experiments.

3. Increasing flow velocity can lead to a sharp increase in the rate of erosion corrosion attack (up to 17X when velocity was increased from 6 ft/s [1.8 m/s] to 13.5 ft/s [4 m/s] in this study). Additionally, the characteristics of the corroded surface can significantly differ demonstrating the role of velocity in material erosion, whether by impingement or dissolved by corrosion reactions.

4. Increase in particle size can cause a severe increase in erosion corrosion rate, all other conditions held constant (aragonite precipitation can definitely).

5. Chlorine disinfectant exacerbated erosion corrosion attack by 4.5 times when compared to the no disinfectant condition due to its high reactivity, and even caused pitting.

6. Presence of the disinfectant chloramine also increased erosion corrosion (1.8X in this case).

This is the first study to successfully demonstrate nonleaded brass erosion corrosion damage in the laboratory. These findings offer new insights into the underlying mechanisms of erosion corrosion that have baffled corrosion scientists for decades, especially because such field failures have never been reproduced in the lab in freshwater systems to the best of our knowledge.

Identical testing done with copper tubes showing negligible damage in the absence of oxygen (Roy and Edwards 2015) indicating the failures to be erosion corrosion (and not just particle impingement induced abrasion). Similar testing is necessary for C46500 to offer a scientifically valid point of comparison with respect to this study.

Furthermore, with several nonleaded brass fittings flooding the market after the enforcement of the Federal Reduction of Lead in Drinking Water Act, there is a need to adequately assess their operational value and longevity. The experimental design offers a promising and rigorous standardized test of erosion corrosion in potable water systems, which can be used for evaluating alloy performance. Future research into these nonleaded materials and associated conditions is warranted to benefit the manufacturers as well as consumers towards better design and choice of alloys for drinking water service.

ACKNOWLEDGEMENTS

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CHAPTER 4. CAVITATION AND EROSION CORROSION RESISTANCE OF NONLEADED PUMP IMPELLER ALLOYS IN CHLORINATED POTABLE WATER

Siddhartha Roy, Philip A. Smith, Gregory R. House, and Marc A. Edwards

ABSTRACT

The January 2014 Federal Reduction of Lead in Drinking Water Act reduced the lead content in brass used in water distribution operations and in premise plumbing from 8% to < 0.25% Pb (termed, "nonleaded") to protect the public from lead exposure. The switch to nonleaded materials has created legitimate concerns for water utilities, because anecdotally, the new nonleaded alloys have sometimes been more susceptible to erosion corrosion than the older leaded brass alloys. This study investigated the performance of 12 nonleaded alloys vis-à-vis conventional leaded Red Brass using an ASTM standard cavitation test and an erosion corrosion pipe-loop method. All 12 nonleaded test alloys were more resistant to cavitation than Red Brass. Silicon Brass C87500 had the greatest susceptibility to erosion corrosion, while stainless steel alloys witnessed negligible weight loss and demonstrated superior resistance to erosion corrosion. All other alloys had erosion corrosion damage comparable to (or worse than) the control red brass. This preliminary study is a critical first step towards determining the useful applications of each material in potable water systems, especially for pump impellers and plumbing fittings exposed to high velocity.

KEYWORDS: cavitation, chlorine, erosion corrosion, nonleaded alloys, potable water, pump impellers, red brass

INTRODUCTION

The era of "nonleaded" alloys used in water distribution operations in the U.S. officially began in January 2014 after the passage of the 2011 Federal Reduction of Lead in Drinking Water Act (SDWA 2011). This new regulation was designed to protect the public from lead exposure and mandated lead levels in alloys not exceed a weighted average of 0.25% of the wetted surface (i.e. the surface that comes in contact with potable water), as opposed to 8% that was legally allowed until the law came into effect. In response, alloy manufacturers have replaced lead in their alloy products with alternatives that include bismuth, selenium, phosphorus, zinc, tin, and aluminum (Daschner 2011, AFS 2015). In addition to reducing lead exposure from the alloys, it was also hoped that their resistance to corrosion and cavitation would be at least as good as the old lead containing alloys (Turkovic et al. 2014; Roy and Edwards 2016).

This shift towards nonleaded materials has created unanticipated challenges for water utilities, because the new alloys were not rigorously performance tested for longevity relative to cavitation or erosion corrosion damage. The AWWA/ANSI E103 "Standard for Horizontal and Vertical Line-Shaft Pumps" lists 11 "lead free" choices under their recommended impeller alloys list (AWWA 2012), but fails to offer guidance on how to select appropriate materials for pumping applications that will not fail prematurely because such data does not exist. This has led to a trial-and-error approach for material selection at utilities, and has already resulted in major increased maintenance costs when the nonleaded impellers fail prematurely (Devries 2014). Impellers may be considered a "canary in the coal mine" relative to failure of other devices, because the high velocities in pumps can cause observable failures in as little as a few months, whereas in other devices a severe and premature failure would not be observed for 5-10 years. The costs of widespread brass plumbing device failures would be extraordinarily high, and it is imperative to better understand these problems as soon as possible.

Reported failures in pump impeller operations

"Red brass" (C83600) has been the most common copper alloy used to manufacture impellers in potable water distribution systems for over 50 years (Devries 2014) and contains 4%-6% lead. Most practical and laboratory based performance data for impellers is for leaded materials like red brass, where the high lead content allowed easy machining of intricate brass devices, sealed potential leaks, and conferred high corrosion resistance of other metals in the alloy resulting in a long service life (Sandvig et al. 2007). The concern is that some of this durability is being lost in newer nonleaded alloys, when additives other than Pb are used.

Selective dissolution (includes dezincification), pitting, stress corrosion cracking, erosion corrosion, and cavitation erosion are the dominant failure mechanisms for copper alloys. For pump impellers used in water distribution systems exposed to severe hydraulic conditions, such as peripheral velocity tip speeds ranging anywhere from 50 to 140 ft/s (or 15-43 m/s), erosion corrosion and cavitation, are the most likely damage modes (Devries 2014). Dezincification (selective leaching of zinc) is also a possibility in some

alloys in certain highly corrosive waters (Sarver 2010, Turkovic et al. 2014) or in certain types of brass with a high propensity for selective zinc leaching. Moreover, a role of chlorine in exacerbating cavitation or erosion corrosion is also strongly suspected (Devries 2014) in nonleaded alloys used as impellers by utilities including the San Jose Water Company (CA), Virgin Valley Water District (NV), and City of Vancouver's Water Department (WA) who witnessed extensive damage in their impeller operations – see Table 4-1 (also, Devries 2014) and Figure 4-1.

Table 4-1. Summary of premature failures of nonleaded brass impellers (Devries 2014)

Utility	**Nonleaded alloy in operation**	**Impeller failure in**	**Chlorine residual (mg/L as Cl_2)**
San Jose Water Co., CA	Low-zinc Silicon Bronze C87600	5-6 years	0.75 mg/L
Virgin Valley Water District, NV	Low-zinc Silicon Bronze C87600	5-6 years	1 mg/L
City of Vancouver's Water Dept., WA	Low-zinc Silicon Bronze and Silicon Bronze	1.5 years; 0.5 years	1 mg/L

Figure 4-1. Pump impeller section (low-zinc silicon bronze) that witnessed extensive short-term damage while in service

The following sections briefly describe the current state of the knowledge with respect to failures by cavitation and erosion corrosion, as well as the effects of chlorine on nonleaded alloys:

Cavitation

Cavitation describes the spontaneous nucleation, growth, and then collapse of gas or vapor bubbles when local hydraulic pressure drops below the gas saturation pressure or below the vapor pressure of water (Novak 2005). Cavitation typically occurs in pump operations when inlet pressure falls below the design inlet pressure of the pump. These conditions lead to formation of vapor bubbles in inlet water near the eye of the impeller which then implode when entering a high pressure zone. Figure 4-2 illustrates some forms of cavitation witnessed in an axial flow impeller (further information about these specific modes can be found in Brennen 2007).

The implosion creates "micro-jets" of water that can travel faster than the speed of sound and with pressures sufficient to physically gouge and damage metallic copper, often causing crater shaped material abrasions inside the system (During 1997, Siegenthaler 2000, Novak 2005, Merkle 2014). Plesset and Chapman (1970) estimated the velocity of the liquid jet, originated at the collapse of the bubble if attached on the solid wall, to be as high as 128 m/s (or 420 ft/s). The micro-jets formed are extremely small and short-lived, but they are still very damaging; in some cases impacting metal surfaces with sufficient force to rip away minute amounts of metal per event (Siegenthaler 2000) and creating major material losses in very short time periods. Vaporous cavitation occurs when the bubble is comprised entirely of water vapor, due to local solution pressure dropping below the vapor pressure and "boiling" the water at ambient temperature. Gaseous cavitation refers to bubbles comprised of dissolved gases and formed by a pressure drop below the saturation pressure of the constituent gases ($p_{fl} < p_g$).

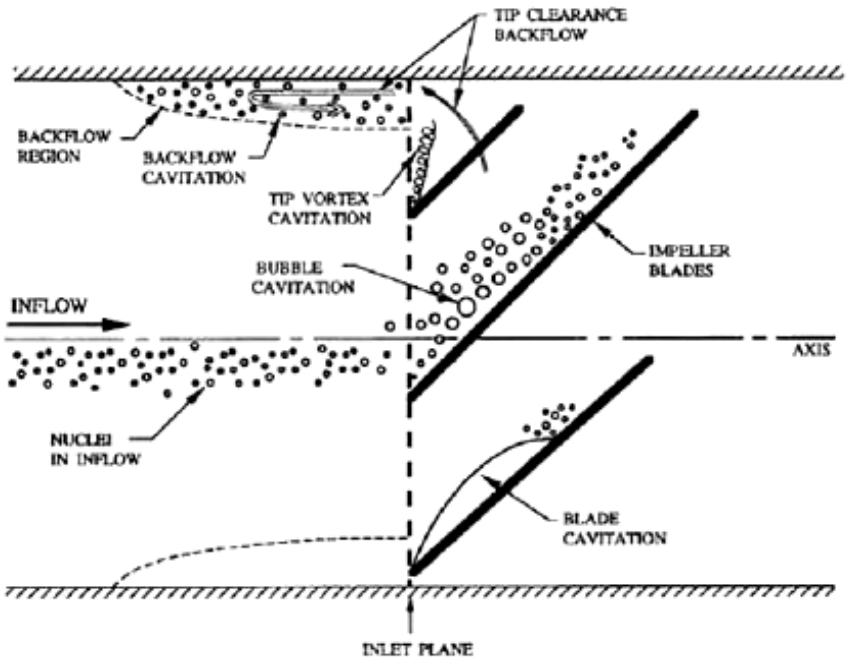

Figure 4-2. Illustrative cavitation types occurring in pump impeller operations (from Brennen 2007; used with permission)

Pure vaporous cavitation is generally more damaging because of the forces involved and localized nature of the problem. Since dissolved gases cushion these implosions, damage from vaporous cavitation would be expected to decrease with higher gas content of the water supply (Jang and Aral 2003).

Furthermore, bubbles are believed to enhance corrosion via gas bubble impingement, bubble implosion from vaporous cavitation, and trapped gas. These cavitation implosions can severely pit the surface of the impeller, degrade pump performance, cause severe instabilities in flow patterns, and shorten its service life (Brennen 2007).

Typical considerations of Net Positive Suction Head required (NPSHr) versus NPSH available (NPSHa) for cavitation do not take the aforementioned complexities into account. Relative resistance to cavitation is, therefore, an important parameter to consider when choosing from a candidate list of nonleaded alloys for high performance and long-lived impellers.

Erosion Corrosion

Erosion corrosion is a form of accelerated localized attack, wherein material is worn away due to rapid flowing liquid that supports corrosion. The phenomenon occurs at high flow rates and is exacerbated by high temperatures, dissolved oxygen, particulates, air bubbles, and factors causing cavitation (Coyne 2009). Pump impellers are exposed to very high localized water velocities which make the alloys used especially subject to erosion corrosion or cavitation.

The majority of testing on nonleaded alloys has focused on simulating freshwater flowing in building plumbing systems where the velocities and associated hydrodynamics are two to three orders of magnitude lower than those encountered in pumping operations in distribution lines and pumping systems. The velocities examined by Turkovic and colleagues, for example, for four nonleaded alloys (see Table 4-2 for details) were 0.5 m/s, 1 m/s and 2 m/s (i.e. 1.6 ft/s, 3.3 ft/s and 6.6 ft/s) to evaluate metal leaching behavior using the European standard method DIN EN 15664-1 (2014). Again, long term resistance to erosion corrosion or cavitation was not tested.

Recent work (Roy and Edwards 2014, Roy and Edwards 2015) has also examined the potentially disastrous role of suspended particulates in exacerbating attack from erosion corrosion, and led to a promising and rigorous standardized test of erosion corrosion as it can occur in potable water. For example, elbows manufactured using nonleaded dezincification resistant (DZR) naval brass (C46500) were tested in pipe loops circulating hard freshwaters with particulates at velocities close to 13 ft/s (4 m/s); these elbows (Figure 4-3) witnessed complete penetration (100% leak) in an alarming two weeks due to suspended particle exacerbated erosion corrosion (Roy and Edwards 2015). By repeating this type of testing for a range of alloys with suitable replication, relative resistance to erosion corrosion can be established.

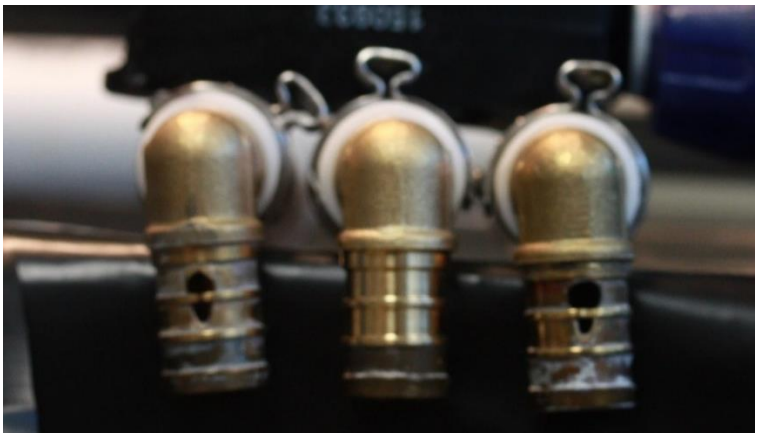

Figure 4-3. Rapid failures in nonleaded brass fittings from a commercial vendor (L-R) pH 7.5 in 13.5 days, pH 7.5 control without particles, pH 10 in 18-19 days

A rigorous assessment of nonleaded alloys for resistance to erosion corrosion in impeller operations using the experimental methods that caused the rapid brass failures discussed above (Roy and Edwards 2015) is, therefore, warranted.

Role of Chlorine Disinfectant

Free chlorine, as a disinfectant, is highly oxidizing, capable of reacting with the protective films that form on alloy surfaces (Sarver 2010). The residual levels encountered by pump impellers can vary from the 0.75 – 1 mg/L to 4 mg/L or even higher (10 – 15 mg/L) when systems are shocked with chlorine to kill bacteria. Exposure to continuous versus intermittent chlorine has been shown to affect corrosion in copper alloys. On the other hand, impingement resistance of alloys varies significantly between alloys in the presence of chlorine (Cohen 2005). Finally, high chlorine residuals in waters can even initiate pitting (Sarver 2010).

In the practical experience of three utilities, leaded brass performed within acceptable Best Efficiency Points (BEPs) for decades without chlorine residuals being a deterrent (Devries 2014). But use of nonleaded low-zinc silicon bronze from leaded brass, however, appears to have resulted in significant thinning and deterioration of the impeller in as little as six months. The susceptibility of the newer nonleaded alloys to residual chlorine in potable water would vary depending on their metallic composition, and associated surface and protective layer characteristics.

Current research in nonleaded alloys in potable water

There has been very little research on corrosion in nonleaded brasses and the experimental conditions mostly aim to study brass fittings in premise plumbing. Cavitation resistance, in fact, has not been tested to the best of our knowledge. Table 4-2 provides a summary of key findings from the literature.

Table 4-2. Summary of research findings on nonleaded brasses in the last decade

Research Study	Summary and Key Findings
Heumann (2006) [extensively examined in Sandvig et al. (2007)]	Two California utilities tested performance of nonleaded brass components, meters, and curb valves in the distribution system. They found "no increase in failures and no significant structural weakening or dealloying" (McNaught et al 2015) when compared to traditional brass.
Turkovic et al. (2014) (Water Research Foundation project)	Evaluation of short term and long term leaching behavior, dezincification resistance, stress corrosion cracking, and erosion corrosion for four nonleaded brasses (C69300 ECO BRASS, C87700 CuZn10Si4MnP, C89520 Envirobrass II, C89844 Federalloy I-844) carried out using standardized methods. Overall, all test alloys performed as good as or better than red brass and were, therefore, "suitable for use in drinking water."
Devries (2014)	Case studies on premature failures in low-zinc silicon bronze pump impellers in three utilities especially in chlorinated water at very high velocities (50-140 ft/s or 15-43 m/s).
McNaught et al. (2015)	Nonleaded corporation stops and angle meter service brass (C89833) valves evaluated over a ten month period using Colorado river water. No significant or accelerated corrosion witnessed.
Roy and Edwards (2016)	Accelerated failures (an alarming two weeks) witnessed for naval brass elbows (C46500) in pipe loops circulating hard water with particulates at 13 ft/s (4 m/s).

Preliminary experiences suggest that nonleaded pump impellers appear to be especially sensitive to erosion corrosion failures (Devries 2014). This is a matter of concern across the industry, because many intricate plumbing devices used in water treatment plants and homes/buildings are constructed from brass, and their premature failure(s) could cause billions of dollars in unanticipated economic losses and damages. Considering the criticality and ubiquity of pump operations in water distribution, and the fact that these components are merely a "tip of the iceberg" for infrastructure assets at risk, there is an urgent need for valuable performance data to the water industry.

In this work, we evaluate the performance of 12 nonleaded alloys and a traditional leaded red brass as a control towards a) cavitation, using the ASTM G32-10 Standard Test Method for Cavitation Erosion Using Vibratory Apparatus, and b) erosion corrosion, using a pipe-loop method (Roy and Edwards 2016) with abrasive suspended solids.

MATERIALS AND METHODS

Test Water

Turkovic and colleagues identified five "corner waters" representing about two-thirds of all distributed drinking water qualities across North America (2014). Synthesized water quality similar to corner water #1 (Hard Water with high chloride content and alkalinity > 300 mg/L as $CaCO_3$) at slightly elevated pH (7.5) and 1-2 mg/L NOM was utilized because it has been established that it causes severe erosion corrosion in both pure copper and nonleaded naval brass C46500 (Roy and Edwards 2015). This choice of hard water is especially favorable because 77% of all community water systems (more than 15 service connections) and more than 95% of all remaining non-community water systems in the United States use groundwater as a drinking water source (US EPA 2012) where high levels of hardness are common (WHO 2011).

Table 4-3 lists the major cations, anions, and other water quality characteristics of the test water. A "worst case scenario" concentration of 4 mg/L as Cl_2 of chlorine disinfectant was initially targeted (and adjusted ~3 times/day throughout the length of each experiment) in test waters to allow for a more accurate assessment of the alloys.

Table 4-3. Test water quality parameters

Parameter	Unit	Value
pH	pH	7.5
Conductivity	uS/cm	810
Dissolved Oxygen	mg/L	8-9
Initial Temperature	°C	20-25
Total alkalinity	mg/L as $CaCO_3$	290
Hardness as $CaCO_3$	mg/L as $CaCO_3$	390
Calcium	mg/L	85
Magnesium	mg/L	44
Sodium	mg/L	37
Silicon	mg/L	14
Potassium	mg/L	1.6
Chloride	mg/L	49
Nitrate	mg/L (NO_3-N)	25
Sulfate	mg/L	66
Free Chlorine	mg/L as Cl_2	< 4

It is acknowledged that testing one water quality type is not necessarily representative of the range of water chemistry characteristics that can contribute to premature corrosion in nonleaded alloys but it is nonetheless a standardized and reproducible test of an aggressive water known to cause erosion corrosion in reasonably short-term experiments of 2 weeks duration.

Test Alloys

Eight nonleaded alloys (including two stainless steel ones) from the ANSI/AWWA E103 standard and four emerging nonleaded materials have been identified for testing alongside conventional leaded red brass as the baseline (Table 4-4). A detailed distribution of elemental percentage values for all 13 alloys extracted from the Copper Development Association database is available in the Appendix (Table A.1).

Table 4-4. Test alloys for this project

No.	Alloy
1	Leaded Red Brass C83600 [CONTROL]
2	Silicon Brass C87500
3	Silicon Bronze C87600
4	Aluminum Bronze C95200
5	Nickel-Aluminum Bronze C95800
6	Tin Bronze C90300
7	Tin Bronze C90700
8	Stainless Steel SS304
9	Stainless Steel SS316
10	ECO BRASS C87850
11	ECO BRASS C87870
12	Federalloy C89833
13	Federalloy C89836

For cavitation, four test specimens (with dimensions of 0.8” x 0.8” x 0.4” OR 2cm x 2cm x 1cm, except for C87870 which was 2cm x 2cm x 0.5cm) were cut from either alloy plates or ingots by a professional workshop technician. Similarly, for erosion corrosion testing, nine specimens (of dimensions: 0.2”x0.2”x2” OR 0.5cm x 0.5cm x 5cm) were cut from each bulk alloy piece for use as replicates in experiments (six for actual testing and three as backup). All specimens were prepared by rinsing with methanol and deionized water respectively. Illustrative test specimens for cavitation and erosion corrosion are shown in Figure 4-4.

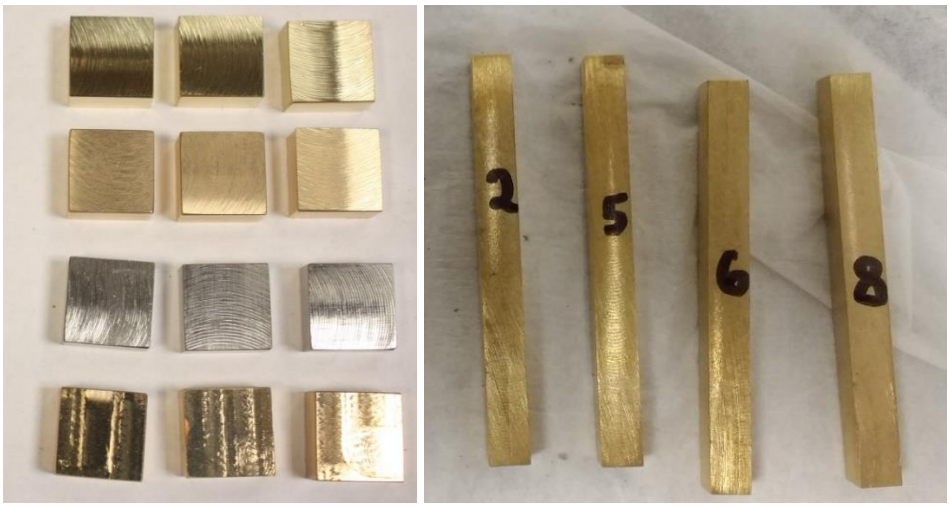

Figure 4-4. Illustrative alloy specimens used in (L) cavitation and (R) erosion corrosion pipe loop experiments (photos not to scale)

Cavitation Test Method

The ASTM G32-10 Standard Test Method for Cavitation Erosion Using Vibratory Apparatus was modified to conduct cavitation experiments using a 500W ultrasonic transducer (hereafter referred to as "cavitator") for alloys listed in Table 4-4. Each specimen was secured at the bottom center of a 1L beaker using copper tube pieces (wrapped in Teflon tape to prevent direct contact with specimen). Test water was freshly prepared prior to each test in a 4 gallon HDPE reservoir; the pH was adjusted to 7.5 using CO_2 gas and 1L was transferred to the test beaker. The beaker was connected to the HDPE reservoir using Silicone tubing and a peristaltic pump (Cole-Parmer) to recirculate test water (at a flow rate ~900 mL/s) and two fans were positioned so as to facilitate speedy dissipation of heat from the "horn" and prevent overheating. This also helped maintain a constant water temperature between 40-44 °C in the beaker. A free chlorine disinfectant residual (of up to 4 mg/L as Cl_2) was maintained throughout the experiment using sodium hypochlorite solution. The chlorine residual was adjusted thrice during the test period (including once at the beginning). It usually stayed between 2-4 mg/L. In rare cases, the residual reached ~ 0.5 mg/L and was raised closer to the 4 mg/L target. These rapid chlorine decay rates can be attributed primarily to high temperatures (Monteiro et al. 2015) presence of NOM, and gas transfer stripping.

The cavitation "horn" tip was positioned 3-5 mm away from the test alloy surface and the cavitator was operated at a power output ~ 330W ± 10W (typically advised range is 250-1000W (ASTM, 2010); the max. possible wattage on this particular model for the modified apparatus was ~370W) with a pulsing 40sec ON/20sec OFF mode. The net runtime of each experiment was 6hr 45min (with total cavitation time of 4hr 30min). Specimen weights were measured three times and their mean calculated using a FisherSci digital balance (up to 4 significant digits) both before and after the experiment. Using this data, percent weight loss was calculated. The modified apparatus is shown in Figure 4-5.

Since the cavitation tips were themselves cavitating rapidly (Bai et al., 2017, Vyas et al. 2017), they were replaced after 4-5 experimental runs (Figure 4-6).

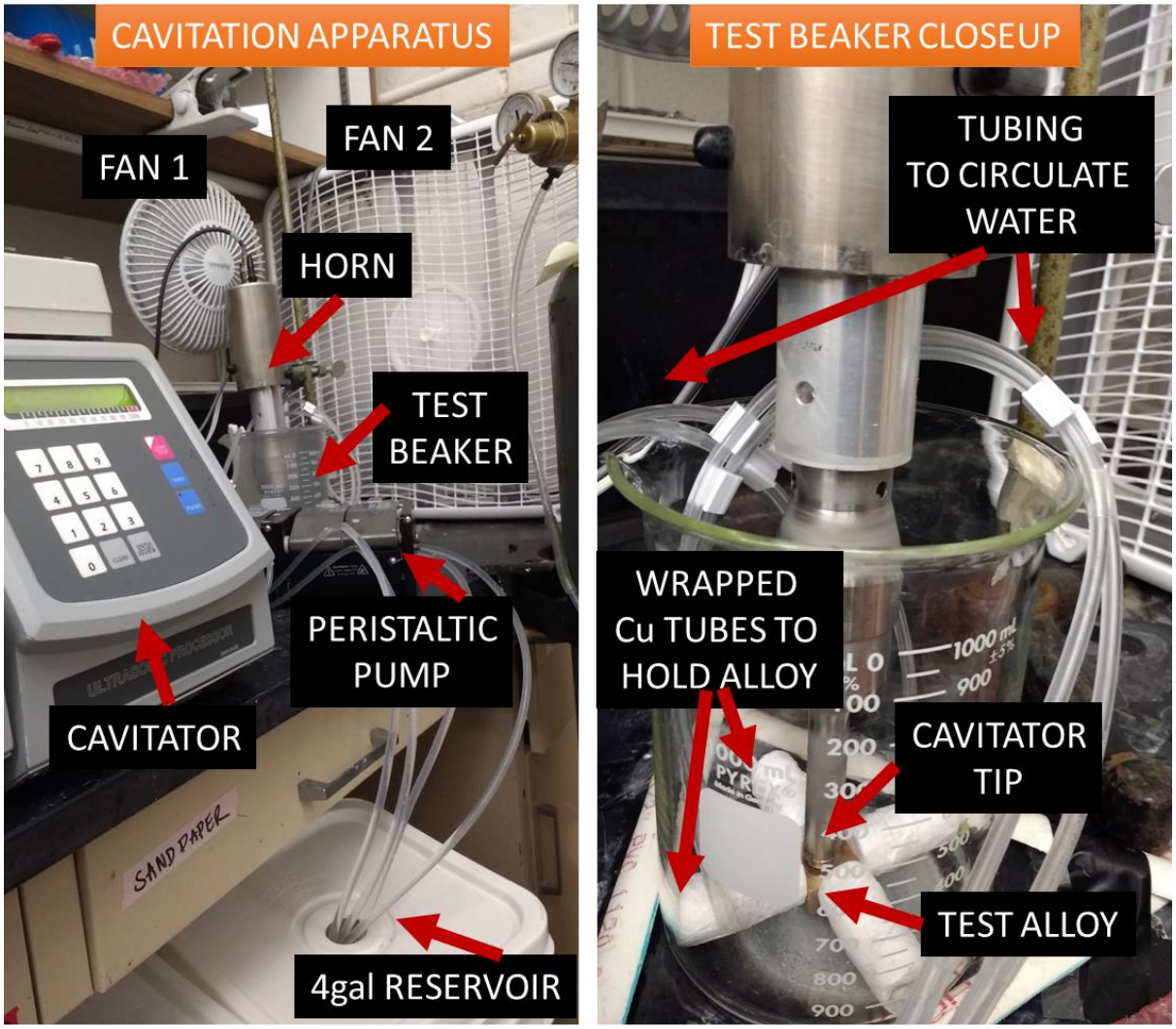

Figure 4-5. Modified ASTM G32-10 Cavitation apparatus

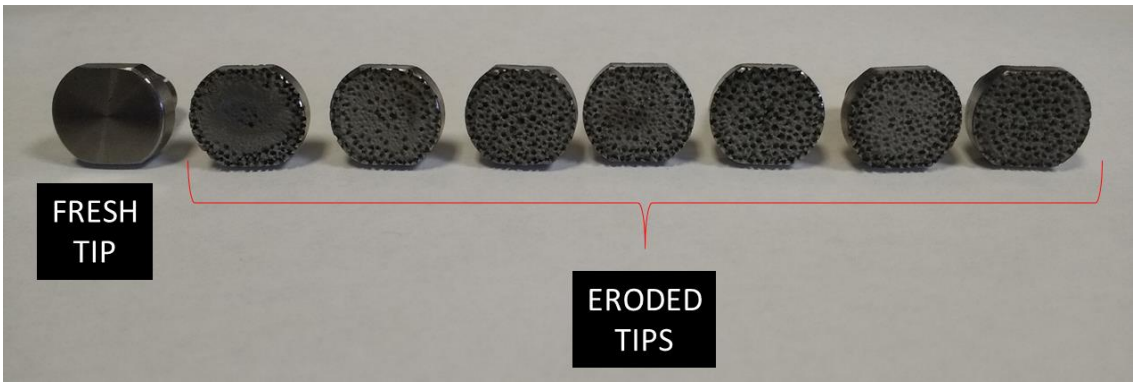

Figure 4-6. Eroded cavitation tips (these were replaced after every 4-5 experimental runs)

Erosion Corrosion Experiment

Three specimens were secured immediately before bends in 4ftx5ft (vertical x horizontal) cross-linked polyethylene (PEX) pipe loops of half-inch diameter (see Figures 4-7 and 4-8) using nylon wire and Teflon tape reinforcements and held in place using steel hose clamps. The PEX pipes were joined using ½" CPVC elbows and Gorilla epoxy glue. Two such rigs were constructed per alloy (i.e., 26 total experimental loops for 6 target alloys and six replicates being tested per alloy).

Test water was freshly prepared using reagent grade chemicals (Fisher Scientific) in a 5-gallon HDPE reservoir. Aragonite particles of size between 1-3 mm (2.5% weight by volume) were added prior to each test. The pH was adjusted to 7.5 using CO_2 gas before starting the experiment (and subsequently adjusted ~3 times/day). A chlorine disinfectant residual of up to 4 mg/L as Cl_2 was targeted at the start, and adjusted ~3 times/day throughout the experiment using sodium hypochlorite solution. Submersible pumps (Superior Pumps Model 91250 ¼ HP) were used to pump water through pipe rigs and water temperatures stayed between 50-60°C, due to the heat generated by the pumps and mechanical energy input of the rig. The net runtime for each experiment was two weeks; water changes were carried out at the end of Week 1 and following any pump failures.

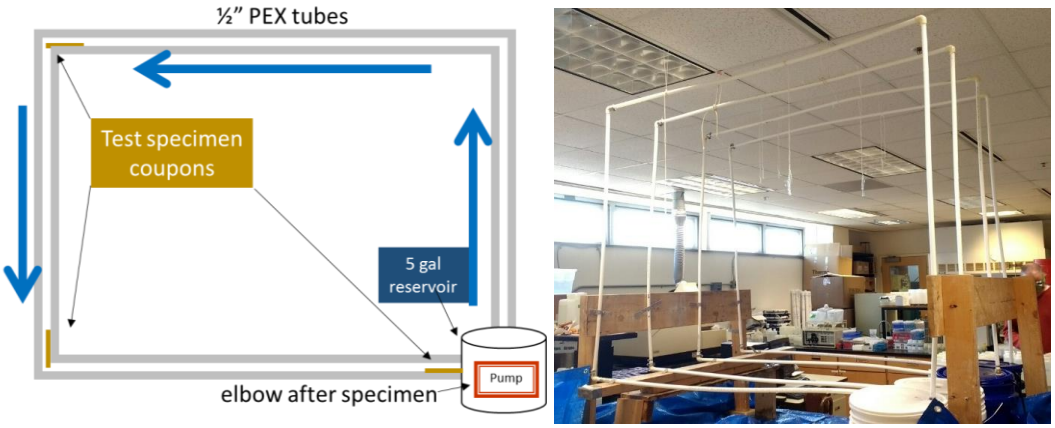

Figure 4-7. (L) Erosion corrosion pipe loop apparatus schematic and (R) Constructed pipe rigs in the laboratory

Figure 4-8. (L) Nylon wires twisted identically around each specimen; (R) Gorilla glue, Teflon tape and steel hose clamps used to make elbow-PEX pipe joint leak-tight.

Specimen weights were measured three times and mean values calculated using a FisherSci digital balance (up to 4 significant digits) before and after the experiment. The alloys were always cleaned using Brasso Metal Polish to remove any rust build-up after the experiments ended prior to weighing. Using this data, percent weight loss was calculated.

RESULTS AND DISCUSSION

Cavitation Test

An analysis of average weight loss results (Figure 4-9) indicates all 12 non-leaded alloys tested were more resistant to cavitation than the control, i.e. leaded red brass. The average percentage weight loss for all alloys did not exceed 0.5% for these short-term tests; considering such minimal weight loss, their relative resistance to cavitation should be treated with caution. It appears that Federalloys C89833 and C89836 and Tin Bronze C90700 may be more prone to cavitation damage than other alloys. Finally, ECO BRASS C87870 actually gained weight following the test, which may be attributed to accumulation of corrosion byproducts. Table A.2 (in the Appendix) offers summary statistics for results shown in Figure 4-9.

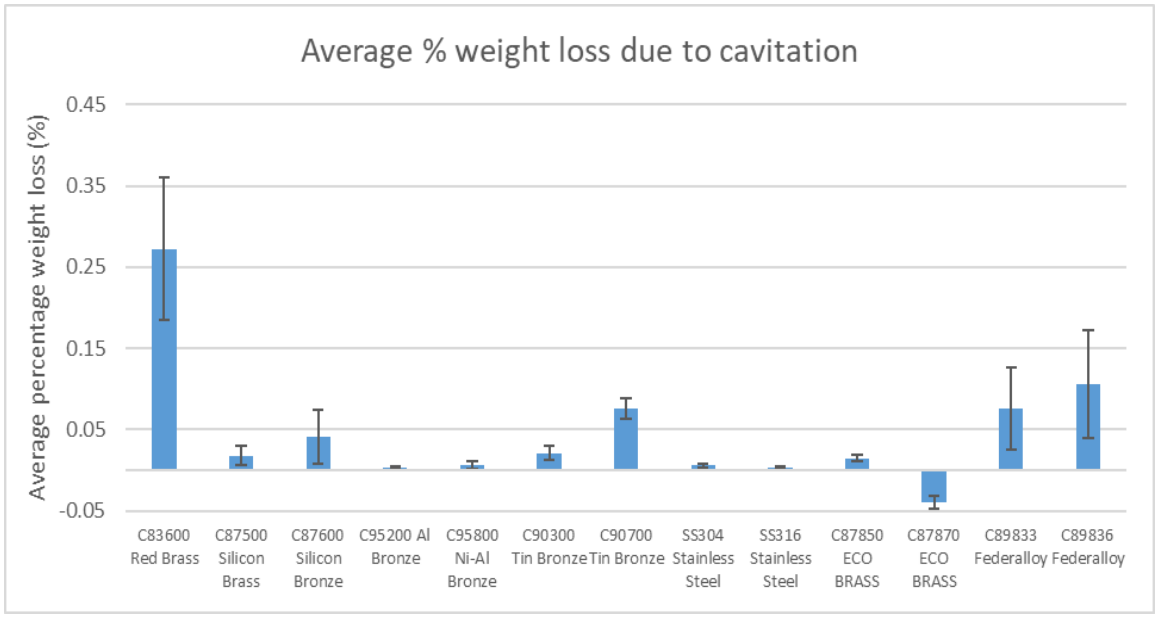

Figure 4-9 Averaged Percentage Weight loss for Cavitation where leaded red brass C83600 is control (extreme left). The error bars indicate standard error.

A visual surface examination of the worst specimen from every triplicate/alloy (Figure 4-10) shows that, indeed, the most pronounced damages are for leaded brass C83600, Federalloy C89833, Federalloy C89836 and Tin Bronze C90700.

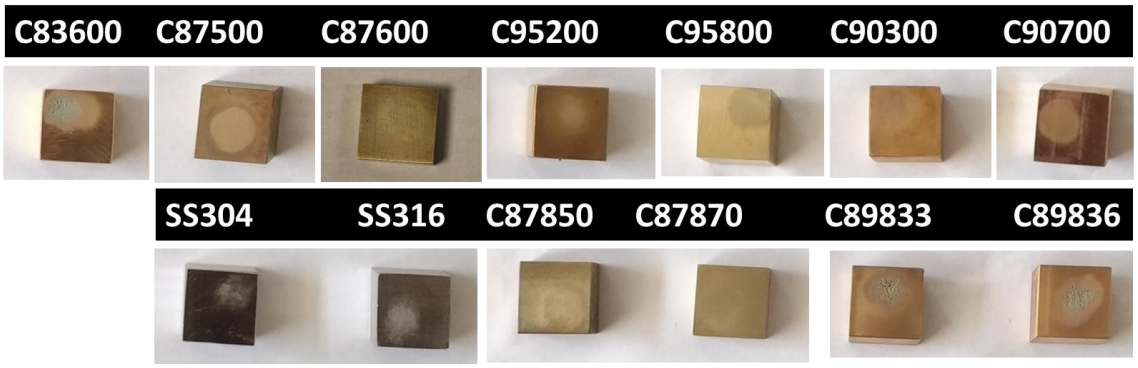

Figure 4-10. Visual of worst cavitation damage for 13 test alloys

Erosion Corrosion Results

An analysis of averaged percent weight loss results indicates differences in performance of all 13 alloys (including the control red brass) when subjected to erosion corrosion (Figure 4-11). Table A.3 (in the Appendix) offers summary statistics for results shown in Figure 4-11.

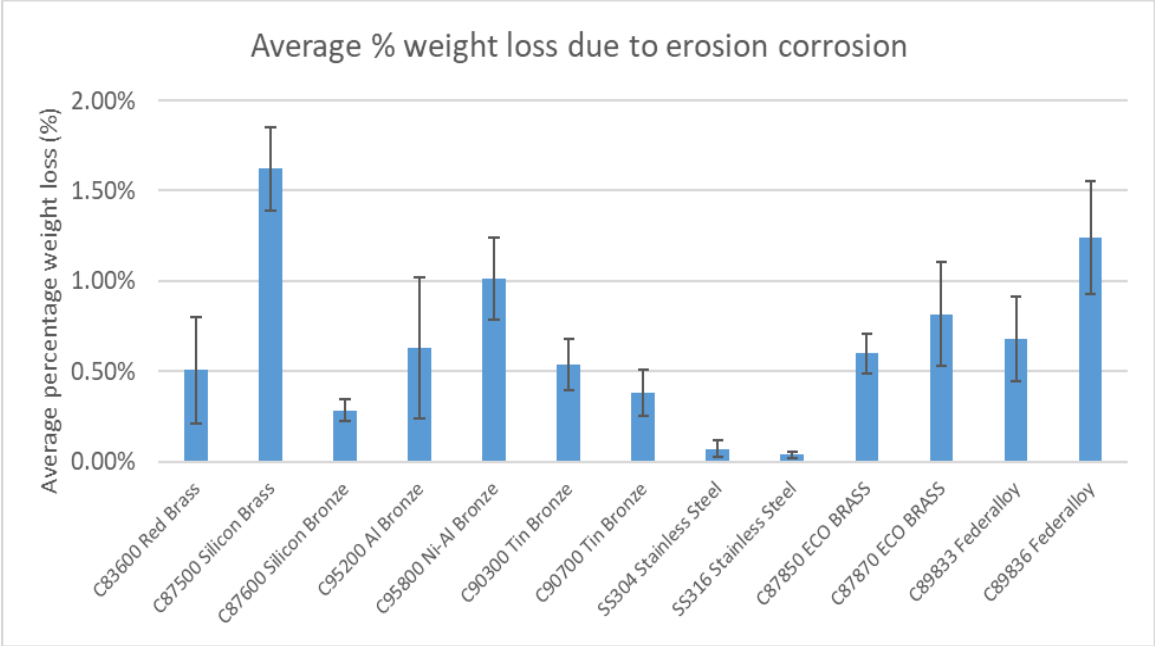

Figure 4-11. Average % Weight Loss for 13 copper alloys subjected to erosion corrosion pipe loop testing for two weeks. The error bars indicate a 95% confidence interval.

The mean % weight loss for the worst performing alloy (Silicon Brass C87500) was 43X higher than that for the best (Stainless Steel or SS316) and 2.4X higher than that for the control (leaded brass C83600). Both stainless steel alloys (SS304 and SS316) had negligible weight loss and demonstrated superior resistance to erosion corrosion vis-à-vis other nonleaded alloys. Most alloys (except both stainless steels SS304 and SS316, and

silicon bronze C87600) showed performance comparable to or worse than the control. Table A.4 (in the Appendix) offers summary statistics for results shown in Figure 4-11.

In terms of statistical significance within the data, performing a single-factor Analysis of Variance (ANOVA) shows that at least one alloy's performance is statistically different than the rest ($p<0.05$; Table A.4 in the Appendix). A Holm-Bonferroni sequential correction statistical test further demonstrates a statistically significant difference between red brass C83600 and silicon brass C87500 (Table A.5 in the Appendix). An alternative way of confirming this is by looking at a box-and-whiskers plot (Figure 4-12) for the data shown in Figure 4-12 where C83600 and C87500 do not overlap.

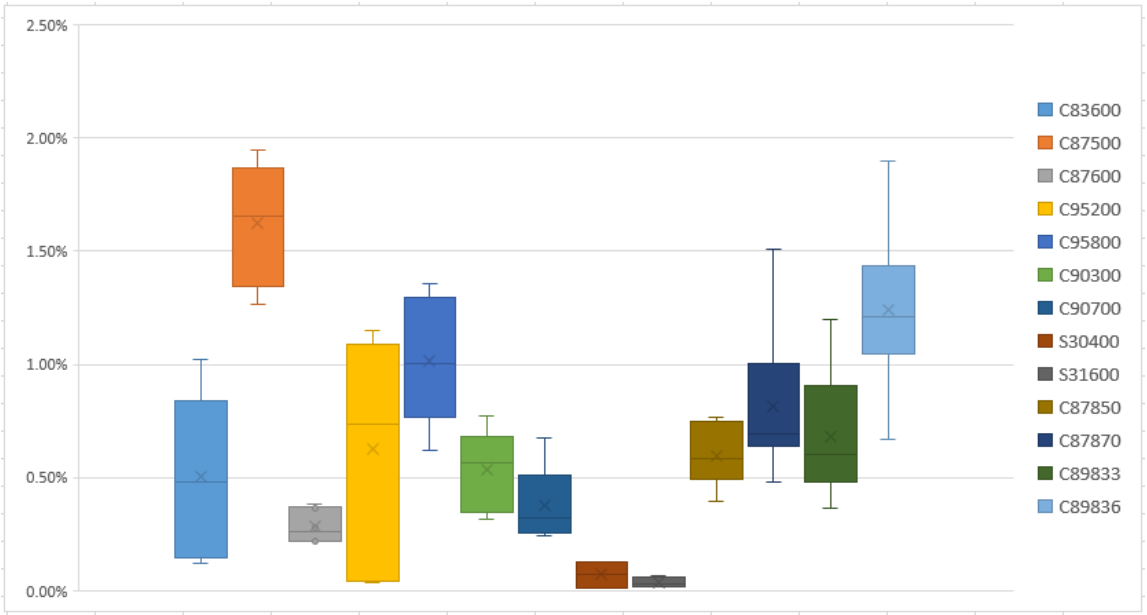

Figure 4-12. Box-and-whiskers plot of % Weight Loss for thirteen copper alloys subjected to erosion corrosion pipe loop testing for two weeks.

Finally, plotting the worst percent weight loss per alloy (Figure 4-13), we get a trend somewhat similar to that seen in Figure 2.8 where both stainless steels (SS316 and SS304) demonstrated the lowest percentage weight loss and silicon brass (C87500) witnessed the highest percentage weight loss demonstrating poor resistance to erosion corrosion. In fact, the percentage weight loss for silicon brass C87500 was 28X that of stainless steel SS316.

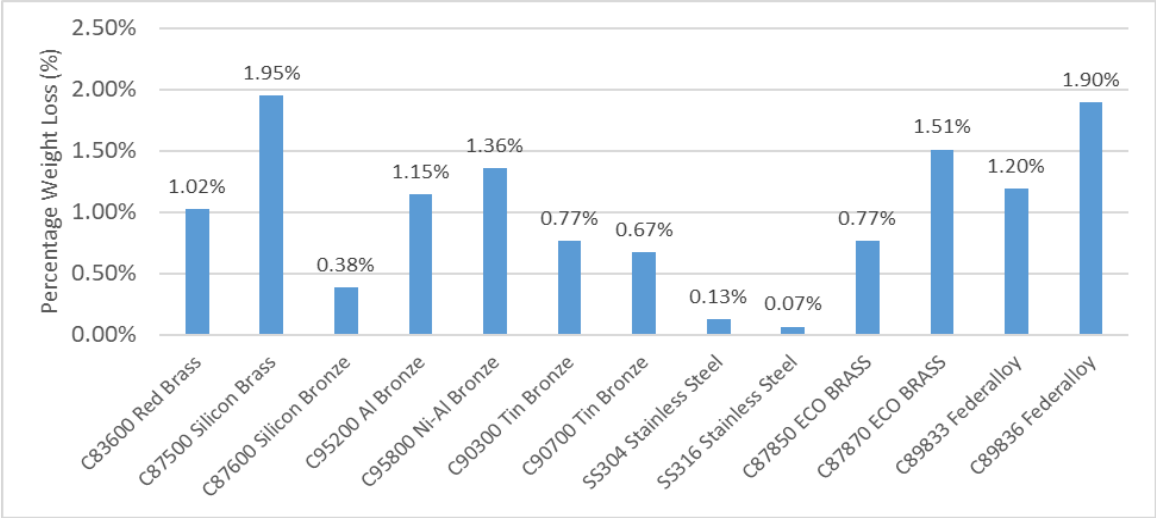

Figure 4-13. Worst percentage weight loss for thirteen copper alloys subjected to erosion corrosion pipe loop testing for two weeks.

A visual surface examination (Figure 4-14) of the worst specimen/alloy shows that almost all conditions (except Stainless Steel) demonstrate the sweeping away of material and absence of corrosion rust, a characteristic of classic erosion corrosion phenomenon. Significant localized damage in the form of wavelet-like patterns are apparent for alloy surfaces of Silicon Brass C87500, Aluminum Bronze C95200, and Federalloy 89836, whereas groove-like formations are clearly visible on the ECO BRASS 87870 (and even Silicon Brass C87500, to some extent) specimen. Figure 4-15 shows close-ups of the damage to alloy surfaces using an Environmental Scanning Electron Microscope (ESEM; Model FEI Quanta 600 FEG). While these images are not representative of overall damage, they do illustrate on a microscopic level, the localized nature of erosion corrosion.

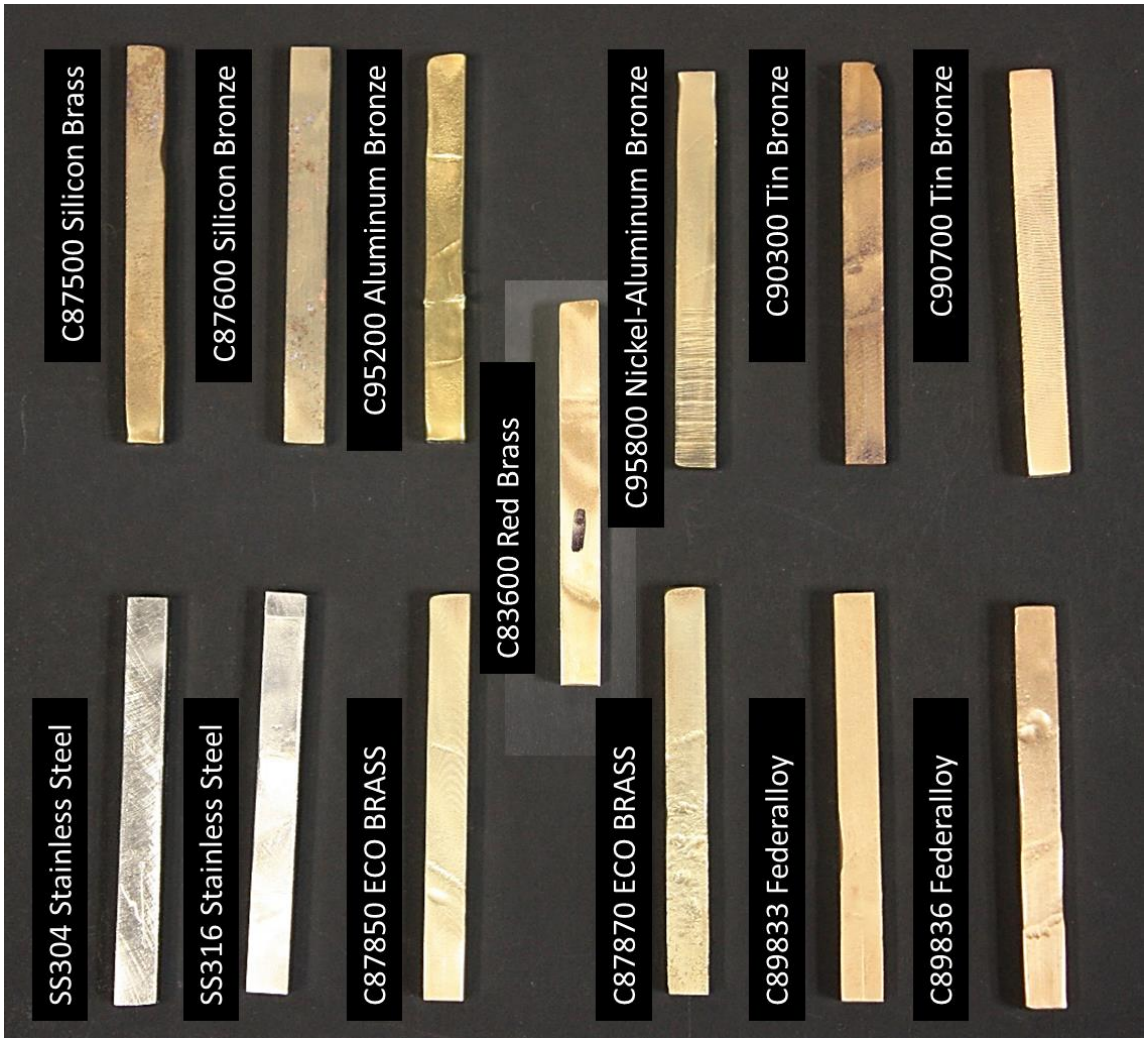

Figure 4-14. Visual comparison of erosion corrosion damage to thirteen copper alloys.

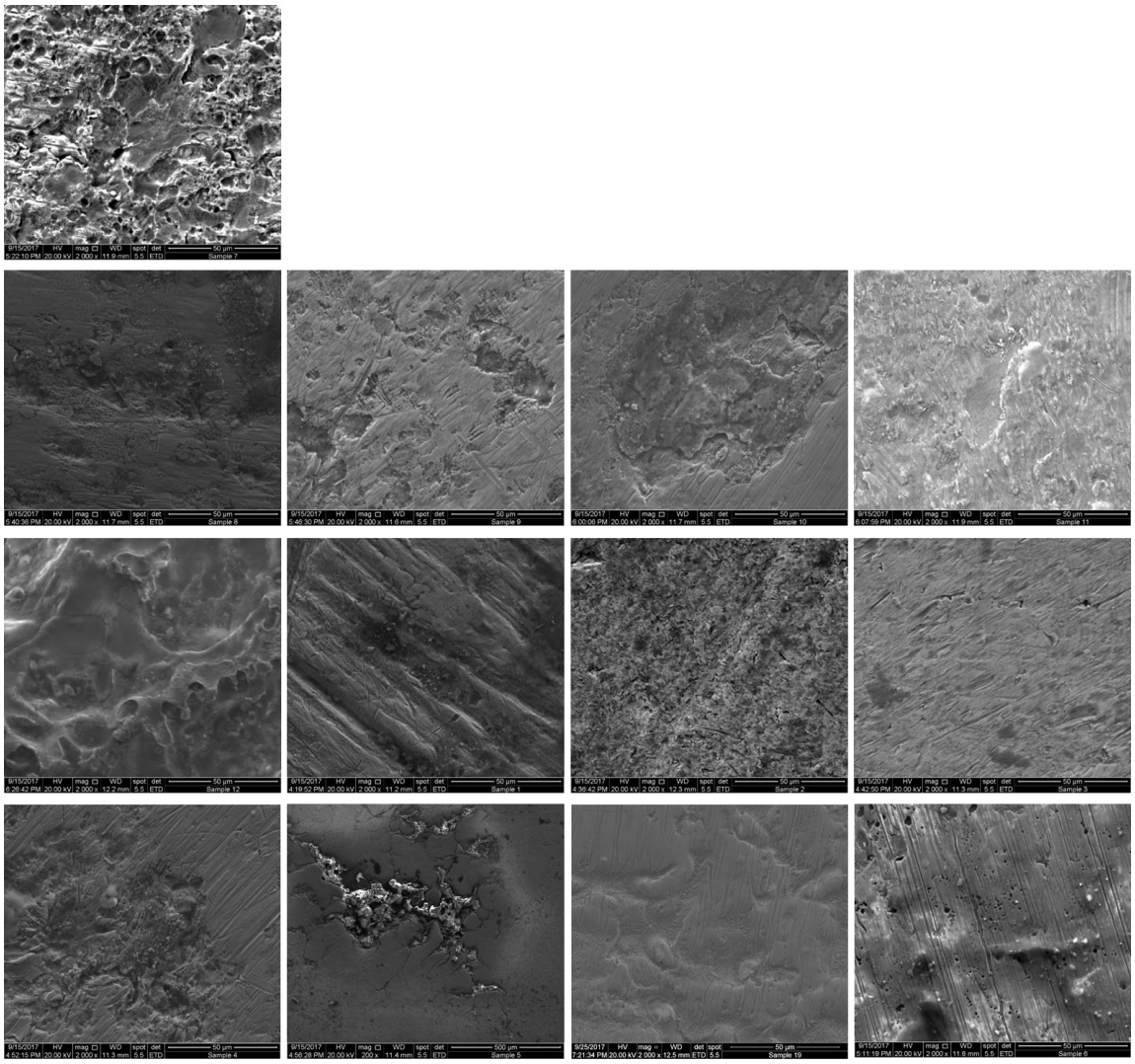

Figure 4-15. Surfaces at the microstructure level of thirteen copper alloys as seen through ESEM at 2000X (except C87870 which is at 200X) to show erosion corrosion damage on a microscopic level. C89833 has been partially modified using PowerPoint to be brighter than captured for clarity.
Row 1: C83600
Row 2: C87500, C87600, C95200, C95800
Row 3: C90300, C90700, SS304, SS316
Row 4: C87850, C87870, C89833, C89836

The unresolved mystery of premature impeller failures

Devries specifically reported premature failures in pump impellers (1.5 – 6 years) manufactured from low-zinc silicon bronze C87600 and C87610 (Table 4-1 and Figure 4-1) being used by three water utilities (2014). In contrast, the performance of C87600 in the current project testing was comparable to or possibly better than red brass C83600. This can possibly be explained in one or more of the following ways:

a) the test methods need optimization with longer testing periods and more replicates to allow adequate time duration for cavitation and erosion corrosion phenomena,
b) corrosion mechanisms beyond cavitation and erosion corrosion, like dezincification or chlorine-induced pitting, could be playing a role,
c) the failed impellers were not manufactured per alloy specifications.

Typically, dezincification is seen in copper alloys with over 15% Zn content (Sarver 2010). However, Rotel and colleagues (2016) do report dezincification in C87600 impellers (~7% Zn content) where dezincified areas had higher proportion of Si. Moreover, higher chlorine (> 1.0 mg/L as free chlorine) is believed to contribute to accelerated erosion corrosion and pitting in silicon bronze C87600 (Murray et al. 2014; Morrow 2015). While high chlorine residual was reasonably maintained in the current testing, it is always possible that longer duration testing might have revealed additional important mechanisms of failure.

Finally, to rule out manufacturing defects, small pieces (< 1 gm) from a damaged impeller (supposedly, C87610, Figure 1.1) and this project's test specimen (C87600) were chemically analyzed using X-Ray Fluorescence (XRF) and an ICP-MS (after acid digestion with nitric and hydrofluoric acid) to confirm their composition (Table 2.3). The XRF comparison showed statistically significant differences, but owing to the XRF device's inability to measure Si (and conflicting values from an XRF reading from an external lab), an ICP-MS analysis was conducted. The ICP-MS values for major elements (including Cu, Zn and Si) for both alloys were within specifications. It appears that the failed impeller met alloy specifications and, therefore, manufacturing defects were not responsible for the accelerated corrosion damage.

Table 4-5. Chemical composition of test alloy and damaged pump impeller measured using XRF and ICP-MS (average of 3 readings per specimen, except external lab values)

	Cu %	**Fe %**	**Zn %**	**Si %**
C87600 specifications	88 min.	< 0.2	4 – 7	3.5 – 5.5
C87610 specifications	90 min.	< 0.2	3 – 5	3 – 5
XRF Analysis				
Test Piece C87600 (FRESH)	92.43	0.27	7.27	Si not measured on this XRF; values are relative weight %
Test Piece C87600 (AFTER EXPERIMENT)	92.49	0.32	7.18	
Impeller Damaged/Exposed Surface	95.40	0.37	4.23	
Impeller Internal Area	95.01	0.19	4.80	
Impeller (external lab)	91	0.02	4.5	4.4
ICP-MS Analysis				
Test Piece	88.5	0.2	6.7	4.5
Impeller	91.2	0.2	4.6	4.1

Study Limitations

The high variability in weight loss results for some alloys can be due to attributed inherent variability within the alloy itself, slight variations in placement in the pipe loop, and the different vertical and horizontal orientations of each triplicate (Figure 4-11). Statistical tests (ANOVA) carried out on weight loss results based on location do demonstrate that one alloy-location combination was more aggressive in causing erosion corrosion than another (a visual distribution of the data by orientation is shown in Figure A.1 in the Appendix). However, based on the number of variables (26 alloy-orientation combinations; 13 alloys and two orientations, either horizontal or vertical), a statistical significance will not help indicate if one orientation is generally worse than another. Finally, the experiments were carried at water temperatures higher than witnessed in distribution systems.

CONCLUSIONS

This study is the first to investigate cavitation and erosion corrosion resistance of twelve nonleaded alloys generating valuable performance data and preliminary recommendations. These findings can improve decision making regarding choice of alloys for a variety of applications, thereby avoiding inappropriate uses and reducing future failures. Results can also be provided to inform brass selection for the AWWA/ANSI E103 Committee for "Standards for Horizontal and Vertical Line-Shaft Pumps".

The following conclusions can generally be drawn from the results:

1. All 12 non-leaded test alloys were more resistant to cavitation than the control, i.e. leaded red brass.
2. The average percentage weight losses for all alloys subjected to the ASTM G32-10 cavitation test were slight (i.e. < 0.5%). Cavitation may not be the dominant failure mechanism at least for some nonleaded pump impellers.
3. Based on visual analysis, Federalloys (C89833 and C89836) and Tin Bronze C90700 may be more prone to cavitation damage than other non-leaded alloys.
4. Red Brass C83600 shows excellent erosion corrosion resistance (<=0.5%) in the pipe loop experiment illustrating its history as the industry standard and an experimental control for comparing relative performance of other alloys
5. Silicon Brass C87500 had the greatest susceptibility to erosion corrosion of the alloys under the conditions tested.
6. Stainless Steel (SS304 and SS316) witnessed negligible weight loss and demonstrated superior resistance to erosion corrosion.

This study was a preliminary evaluation of the relative resistance of the nonleaded alloys to cavitation and erosion corrosion damage. Future studies could reach more definitive conclusive results with longer duration studies and more replicates.

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SUPPLEMENTARY DATA AND FIGURES

Table A.1. Test Alloys and Major Constituent Elements (Elemental % values from the Copper Development Association's and AZOM's databases)

Alloy	Copper (%)	Lead (%)	Zinc (%)	Others (%)
Leaded Red Brass C83600	84-86	4-6	4-6	4-6% Sn
Silicon Brass C87500	79	<0.09	12-16	<0.5% Al, 3-5% Si
Silicon Bronze C87600	> 88	<0.09		<0.2% Fe, <0.25% Mn, 3.5-5.5% Si
Aluminum Bronze C95200	> 86			2.5-4% Fe, 8.5-9.5% Al
Nickel-Aluminum Bronze C95800	> 79	< 0.03		<0.1% Si, 0.8-1.5% Mn, 3.5-4.5% Fe, 4-5% Ni, 8.5-9.5% Al
Tin Bronze C90300	86-89	< 0.3	3-5	<0.005% Al, <0.005% Si, <0.05% P, <0.05% S, <0.2% Fe, <0.2% Sb, <1.0% Ni, 7.5-9.0% Sn
Tin Bronze C90700	88-90	< 0.5	< 0.5	<0.005% Al, <0.005% Si, <0.05% S, <0.15% Fe, <0.2% Sb, <0.3% P, <0.5% Ni, 10-12% Sn
Stainless Steel SS304 (S30400)				Fe (remaining), <0.08% C, 17.5-20% Cr, 8-11% Ni, <2% Mn, <1% Si, <0.045% P, <0.03% S
Stainless Steel SS316 (S31600)				Fe (remaining), <0.03% C, 16-18.5% Cr, 10-14% Ni, 2-3% Mo, <2% Mn, <1% Si, <0.045% P, <0.03% S
ECO BRASS C87850	74-78	<0.09	Remaining	0.05-0.2% P, 0.1% Fe, <0.1% Mn, <0.1% Sb, <0.2% Ni, <0.3% Sn, 2.7-3.4% Si
ECO BRASS C87870	75-79	<0.09	16-23	<0.03% Zr, 0.05-2.0% P, <0.1% Fe, <0.1% Mn, <0.2% Ni, 0.3-0.7% Sn
Federalloy C89833	86-91	<0.09	2-6	<0.005% Al, <0.005% Si , <0.05% P, <0.08% S, <0.25% Sb, <0.3% Fe, <1% Ni, 1.7-2.7% Bi, 4-6% Sn
Federalloy C89836	87-91	<0.25	2-4	<0.005% Si, <0.06% P, <0.08% S, <0.25% Sb, <0.35% Fe, <0.9% Ni, 1.5-3.5% Bi, 4-7% Sn

Table A.2. Summary Statistics for Cavitation experiments

Alloy (n=3 for all)	Alloy #	Average % Weight Loss	Std Dev	Std Error
Leaded Brass	C83600	0.2724	0.1520	0.0877
Silicon Brass	C87500	0.0182	0.0203	0.0117
Silicon Bronze	C87600	0.0416	0.0572	0.0331
Aluminum Bronze	C95200	0.0040	0.0018	0.0011
Nickel Aluminum Bronze	C95800	0.0066	0.0083	0.0048
Tin Bronze	C90300	0.0213	0.0146	0.0084
Tin Bronze	C90700	0.0756	0.0217	0.0125
Stainless Steel	SS304	0.0059	0.0036	0.0021
Stainless Steel	SS316	0.0028	0.0033	0.0019
ECO BRASS	C87850	0.0147	0.0070	0.0041
ECO BRASS	C87870	-0.0394	0.0138	0.0080
Federalloy	C89833	0.0757	0.0880	0.0508
Federalloy	C89836	0.1059	0.1157	0.0668

Table A.3. Summary Statistics for Erosion Corrosion experiments

Alloy (n=6 for all)	Alloy #	Average % Weight Loss	Std Dev	Std Error
Leaded Brass	C83600	0.5053	0.003676	0.001501
Silicon Brass	C87500	1.6218	0.002876	0.001174
Silicon Bronze	C87600	0.2840	0.000743	0.000303
Aluminum Bronze	C95200	0.6290	0.004869	0.001988
Nickel Aluminum Bronze	C95800	1.0131	0.002823	0.001152
Tin Bronze	C90300	0.5373	0.001797	0.000734
Tin Bronze	C90700	0.3793	0.001623	0.000662
Stainless Steel	SS304	0.0700	0.000587	0.000239
Stainless Steel	SS316	0.0377	0.000226	9.23E-05
ECO BRASS	C87850	0.5987	0.001379	0.000563
ECO BRASS	C87870	0.8174	0.003577	0.00146
Federalloy	C89833	0.6819	0.002938	0.001199
Federalloy	C89836	1.2396	0.003912	0.001597

Table A.4. ANOVA Table for Erosion Corrosion results
(F > Fcrit; we therefore reject the null hypothesis that all means are equal)

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
C83600	6	0.03032	0.005053	1.35E-05		

C87500	6	0.097311	0.016218	8.27E-06		
C87600	6	0.017038	0.00284	5.52E-07		
C95200	6	0.037739	0.00629	2.37E-05		
C95800	6	0.060786	0.010131	7.97E-06		
C90300	6	0.032236	0.005373	3.23E-06		
C90700	6	0.022757	0.003793	2.63E-06		
S30400	6	0.004199	0.0007	3.44E-07		
S31600	6	0.002259	0.000377	5.11E-08		
C878750	6	0.035924	0.005987	1.9E-06		
C87870	6	0.049042	0.008174	1.28E-05		
C89833	6	0.040913	0.006819	8.63E-06		
C89836	6	0.074376	0.012396	1.53E-05		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.001445	12	0.00012	15.82683	5.82E-15	1.90437
Within Groups	0.000495	65	7.61E-06			

Table A.5. Holm-Bonferroni Sequential Correction Calculations for Erosion Corrosion Results

Comparison	**Levene's Variance Test Hypothesis Testing**	**p-values from independent t-tests**	**Holm Rank**	**p'**	**Holm-Bonferroni p-value**	**Outcome**
C83600 vs C87500	Fail to reject	0.000159637	1	0.001916	0.004166667	Significant
C83600 vs C89836	Fail to reject	0.007363816	2	0.081002	0.004545455	Not Significant
C83600 vs C95800	Fail to reject	0.022960483	3	0.229605	No further comparisons allowed	Not Significant
C83600 vs SS316	Reject	0.026283624	4	0.236553		Not Significant
C83600 vs SS304	Reject	0.033278026	5	0.266224		Not Significant
C83600 vs C87870	Fail to reject	0.16704587	6	1.169321		Not Significant
C83600 vs C87600	Reject	0.203641095	7	1.221847		Not Significant
C83600 vs C89833	Fail to reject	0.379740538	8	1.898703		Not Significant

C83600 vs C90700	Reject	0.467883649	9	1.871535		Not Significant
C83600 vs C878750	Reject	0.580065062	10	1.740195		Not Significant
C83600 vs C95200	Fail to reject	0.630303821	11	1.260608		Not Significant
C83600 vs C90300	Reject	0.853599361	12	0.853599		Not Significant

Note: Independent t-tests with 95% confidence interval were performed for each comparison set. This was followed by the Holm-Bonferroni Sequential Correction Calculation.

Table A.6 ANOVA Table for Erosion Corrosion results by orientation (F > Fcrit; we therefore reject the null hypothesis that all means are equal)

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
83600-H	4	0.022648	0.005662	1.64E-05		
83600-V	2	0.007672	0.003836	1.38E-05		
87500-H	4	0.060557	0.015139	9.13E-06		
87500-V	2	0.036754	0.018377	4.31E-09		
87600-H	4	0.010391	0.002598	5.09E-07		
87600-V	2	0.006647	0.003324	5.32E-07		
95200-H	4	0.019583	0.004896	2.99E-05		
95200-V	2	0.018156	0.009078	5.45E-06		
95800-H	4	0.03984	0.00996	9.65E-06		
95800-V	2	0.020946	0.010473	1.06E-05		
90300-H	4	0.022153	0.005538	3.83E-06		
90300-V	2	0.010083	0.005041	4.32E-06		
90700-H	4	0.014915	0.003729	4.07E-06		
90700-V	2	0.007842	0.003921	8.92E-07		
SS304-H	4	0.00288	0.00072	4.03E-07		
SS304-V	2	0.001319	0.000659	5.06E-07		
SS316-H	4	0.001377	0.000344	3.95E-08		
SS316-V	2	0.000882	0.000441	1.25E-07		
87850-H	4	0.024634	0.006159	2.96E-06		
87850-V	2	0.01129	0.005645	2.78E-07		
87870-H	4	0.027019	0.006755	2.1E-06		
87870-V	2	0.022023	0.011012	3.35E-05		
89833-H	4	0.023583	0.005896	3.75E-06		

89833-V	2	0.01733	0.008665	2.17E-05		
89836-H	4	0.043445	0.010861	7.95E-06		
89836-V	2	0.030931	0.015466	2.44E-05		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.001551	25	6.2E-05	8.308431	9.06E-11	1.718753
Within Groups	0.000388	52	7.47E-06			

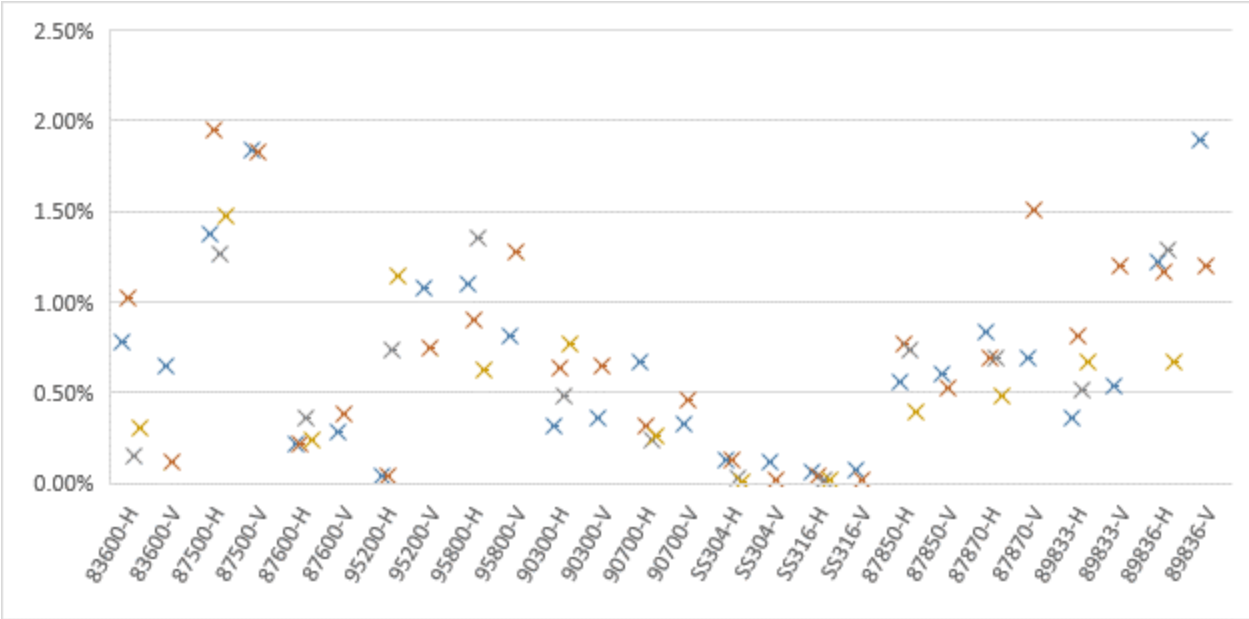

Figure A.1. Distribution of weight loss data by orientation per alloy

CHAPTER 5. KEY INTELLECTUAL CONTRIBUTIONS, AUTHOR CONTRIBUTIONS, CONCLUSIONS, RECOMMENDATIONS AND FUTURE RESEARCH NEEDS

Siddhartha Roy and Marc A. Edwards

KEY INTELLECTUAL CONTRIBUTIONS

The technical work in Chapters 1-4 makes the following key intellectual contributions:

1) This is the first work to critically review the erosion corrosion literature, by putting prior work into context, synthesizing plumbing standards and building codes, and making recommendations for future work to explore erosion corrosion mechanisms. Such research is timely, given that recent Legionella Risk Management guidelines in hot water recirculation systems and use of new lead free plumbing materials, might alter the likelihood of erosion corrosion failures (Chapter 1).
2) It refutes the conventional wisdom that hard waters are not prone to causing pipe failures, by providing compelling evidence of hard water aggressiveness through a) laboratory studies accurately mimicking field failures, and b) a forensic investigation of actual building leaks and pipe damage in a high profile case that occurred in the San Francisco Bay Area (Chapter 2).
3) After decades of failure to replicate rapid erosion corrosion in the laboratory as it occurs in the field, we developed a test protocol that creates fully penetrating leaks in a new copper pipe in as little as 13.5 days, if high levels of particulates created in certain hard waters are present. This sets the stage for reproducible, relatively short-term laboratory studies, to systematically evaluate particle-induced erosion corrosion problems (Chapter 2).
4) Specifically, this work devises an accelerated erosion corrosion test (pipe-loop with aggressive water chemistry and entrained particulates) to study rates of erosion corrosion as a function of materials (copper, nonleaded brasses, nonleaded bronzes, emerging copper-based alloys and stainless steels) used in drinking water supply infrastructure, at normal temperatures, water velocities and chemistries. This test protocol is of tremendous practical and scientific value (Chapter 3).
5) One illustrative application of this test is to reveal chemical mechanisms of attack, including the ability to isolate key water chemistry parameters that contribute to erosion corrosion. Tests with low levels of dissolved oxygen prove that the mechanism of attack is predominantly erosion corrosion, not erosion alone (Chapters 2 and 3).
6) A second illustrative application of this test is to evaluate alloys used in potable water infrastructure, including a head-to-head comparison of 12 emerging nonleaded alloys vis-à-vis traditional red brass, and ranking their relative resistance to both cavitation and erosion corrosion (Chapter 4).

AUTHOR CONTRIBUTIONS

Author initials: *SR = Siddhartha Roy; MAE = Marc A. Edwards; PS = Philip Smith; GRH = Gregory R. House; JMC = Jeff M. Coyne, and JAN = Julia Ann Novak.*

SR and MAE designed research; SR, PS and GRH performed research; SR analyzed data; JMC and JAN contributed review sections from past work; SR and MAE co-authored research papers/dissertation chapters. The content is the sole responsibility of the authors and does not necessarily represent the official views of funding agencies, including the Copper Development Association, San Jose Water Company, and Water Research Foundation.

CONCLUSIONS

1) Erosion corrosion occurs due to a complex interplay of hydrodynamics and electrochemical reactions between water, suspended particulates and metals;
2) The "flow-induced failures" framework arising from our comprehensive literature review, includes mechanisms of concentration cell corrosion, gaseous cavitation, particle impingement, high velocity water impingement;
3) During long term (3-7 month testing), hard waters without suspended particulates, are equally, if not more aggressive, than soft waters in causing erosion corrosion;
4) Long term testing for potable water at 5-15X recommended velocities and at higher temperatures alone, is unable to reproduce rapid field failures, contrary to predictions of prior research;
5) Particles, especially precipitating calcium carbonate hardness as aragonite, cause very rapid erosion corrosion of copper pipe and nonleaded brass fittings, with fully penetrating leaks in as little as 13.5 days;
6) For potable water with suspended particulates, velocity is a critical parameter in determining effect of particles on pipe walls;
7) Failures are more pronounced in high turbulence areas, like bends, but long straight sections of copper tube are also attacked, despite using operating conditions and water chemistries consistent with plumbing codes;
8) Qualitatively, lowering pH, increasing flow velocity, increasing water temperatures, entrainment of particles (and of bigger sizes), and addition of chlorine disinfectant, increases the rate of erosion corrosion;
9) All nonleaded test alloys are more resistant to cavitation than the control, i.e. leaded red brass. Based on visual analysis, Federalloys (C89833 and C89836) and Tin Bronze C90700 may be more prone to cavitation damage than other non-leaded alloys;
10) Silicon Brass C87500 has the greatest susceptibility to erosion corrosion of the alloys;
11) Stainless Steel (SS304 and SS316) demonstrates superior resistance to erosion corrosion.

RECOMMENDATIONS

Water Utilities. If a water utilities provides very hard water (over 300 mg/L as $CaCO_3$) to customers, utilities might want to consider practical testing of scaling propensity, to determine the likelihood of forming particulate calcium carbonate in water heaters as a function of temperature. If problems are significant enough, perhaps anti-scalants should be considered. In some waters with an unusually high propensity for cavitation and erosion corrosion, investments in stainless steel impellers may be warranted.

Building Owners and Construction Companies. If particles are a problem at the point of entry to your building (turbid water or clogging as an indicator), a screening filter may help decrease turbidity and, thus, potential particle-induced erosion corrosion problems. If you receive very hard water, you can install a softener at the building's point-of-entry to decrease the propensity of limestone fouling, as well as hard particles precipitating as crystals and damaging your plumbing system. It might be possible to settle or filter suspended scale particulates from the system to reduce the likelihood of damage, especially in recirculating systems. Generally speaking, following Copper Development Association's recommendation of 2-3 ft/s for most systems with copper pipes, is adequate (CDA 2016). However, in some waters, flow rates of even 20 ft/s do not appear to create problems. More research is needed on the water chemistries that create such problems. When enforcing ASHRAE Legionella Risk Management guidelines for your building, avoid thermal shock treatment (the guideline emphasizes temperatures above 77°C) and shock chlorination strategies, unless absolutely essential (ASHRAE 2015). Increased temperatures may also contribute to faster scaling, as calcium becomes less soluble with increasing temperature.

FUTURE WORK

Future research should examine the effects of lower, more realistic, particle concentrations and how they affect erosion corrosion rates. The effects of adding trace sequestering agents such as phosphate or polyphosphate in possibly preventing formation of solids, hindering aging from soft calcium carbonate to harder crystals such as aragonite by the process of crystal poisoning (Stumm and Morgan, 1996) and reducing erosion corrosion should be another relevant focus area.

The nonleaded alloys comparative study (Chapter 4) shows high variability in performance of some alloys. This can be attributed to inherent variability within the alloy itself, slight variations in their placement in pipe loops, and the different vertical and horizontal orientations of each replicate. These limitations can be overcome with longer duration studies, more replicates and also specifically investigating alloy orientations (vertical vs. horizontal) with additional replicates.

Replication of this work (e.g., for copper pipes at multiple velocities) will help accurately relate corrosion rates with velocity exponent using the widely accepted relationship: corrosion rate α $(vel)^b$; where, v = bulk water velocity and b = velocity exponent (Postlethwaite and Nesic 2011). Some consideration should be given to computational

fluid dynamic modeling to explicitly correlate localized turbulence factors (measured using dimensionless numbers including Reynolds Number, Schmidt Number and Sherwood Number) with the flow-induced damage.

Retrospective studies should examine the hypothesis that precipitated particulates like crystalline aragonite in hard water may have caused accelerated pipe damage, especially as aragonite at high concentrations is being found in scales deposited on hot water pipe walls (e.g., Hafid et al. 2015).

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CHAPTER 5. ACADEMIC RESEARCH IN THE 21ST CENTURY: MAINTAINING SCIENTIFIC INTEGRITY IN A CLIMATE OF PERVERSE INCENTIVES AND HYPERCOMPETITION

Marc A. Edwards and Siddhartha Roy

ABSTRACT

Over the last 50 years, we argue that incentives for academic scientists have become increasingly perverse in terms of competition for research funding, development of quantitative metrics to measure performance, and a changing business model for higher education itself. Furthermore, decreased discretionary funding at the federal and state level is creating a hypercompetitive environment between government agencies (e.g., EPA, NIH, CDC), for scientists in these agencies, and for academics seeking funding from all sources—the combination of perverse incentives and decreased funding increases pressures that can lead to unethical behavior. If a critical mass of scientists become untrustworthy, a tipping point is possible in which the scientific enterprise itself becomes inherently corrupt and public trust is lost, risking a new dark age with devastating consequences to humanity. Academia and federal agencies should better support science as a public good, and incentivize altruistic and ethical outcomes, while de-emphasizing output.

KEYWORDS: academic research; funding; misconduct; perverse incentives; scientific integrity

INTRODUCTION

The incentives and reward structure of academia have undergone a dramatic change in the last half century. Competition has increased for tenure-track positions, and most U.S. PhD graduates are selecting careers in industry, government, or elsewhere partly because the current supply of PhDs far exceeds available academic positions (Cyranoski et al., 2011; Stephan, 2012a; Aitkenhead, 2013; Ladner et al., 2013; Dzeng, 2014; Kolata, 2016). Universities are also increasingly "balance<ing> their budgets on the backs of adjuncts" given that part-time or adjunct professor jobs make up 76% of the academic labor force, while getting paid on average $2,700 per class, without benefits or job security (Curtis and Thornton, 2013; U.S. House Committee on Education and the Workforce, 2014). There are other concerns about the culture of modern academia, as reflected by studies showing that the attractiveness of academic research careers decreases over the course of students' PhD program at Tier-1 institutions relative to other careers (Sauermann and Roach, 2012; Schneider et al., 2014), reflecting the overemphasis on quantitative metrics, competition for limited funding, and difficulties pursuing science as a public good.

In this article, we will (1) describe how perverse incentives and hypercompetition are altering academic behavior of researchers and universities, reducing scientific progress and increasing unethical actions, (2) propose a conceptual model that describes how emphasis on quantity versus quality can adversely affect true scientific progress, (3) consider ramifications of this environment on the next generation of Science, Technology, Engineering and Mathematics (STEM) researchers, public perception, and the future of science itself, and finally, (4) offer recommendations that could help our scientific institutions increase productivity and maintain public trust. We hope to begin a conversation among all stakeholders who acknowledge perverse incentives throughout academia, consider changes to increase scientific progress, and uphold "high ethical standards" in the profession (NAE, 2004).

PERVERSE INCENTIVES IN RESEARCH ACADEMIA: THE NEW NORMAL?

When you rely on incentives, you undermine virtues. Then when you discover that you actually need people who want to do the right thing, those people don't exist…—Barry Schwartz, Swarthmore College (Zetter, 2009)

Academics are human and readily respond to incentives. The need to achieve tenure has influenced faculty decisions, priorities, and activities since the concept first became popular (Wolverton, 1998). Recently, however, an emphasis on quantitative performance metrics (Van Noorden, 2010), increased competition for static or reduced federal research funding (e.g., NIH, NSF, and EPA), and a steady shift toward operating public universities on a private business model (Plerou, et al., 1999; Brownlee, 2014; Kasperkevic, 2014) are creating an increasingly perverse academic culture. These changes may be creating problems in academia at both individual and institutional levels (Table 6-1).

Table 6-1. Growing Perverse Incentives in Academia

Incentive	***Intended effect***	***Actual effect***
"Researchers rewarded for increased number of publications."	"Improve research productivity," provide a means of evaluating performance.	"Avalanche of" substandard, "incremental papers"; poor methods and increase in false discovery rates leading to a "natural selection of bad science" (Smaldino and Mcelreath, 2016); reduced quality of peer review
"Researchers rewarded for increased number of citations."	Reward quality work that influences others.	Extended reference lists to inflate citations; reviewers request citation of their work through peer review
"Researchers rewarded for increased grant funding."	"Ensure that research programs are funded, promote growth, generate overhead."	Increased time writing proposals and less time gathering and thinking about data. Overselling positive results and downplay of negative results.
Increase PhD student productivity	Higher school ranking and more prestige of program.	Lower standards and create oversupply of PhDs. Postdocs often required for entry-level academic positions, and PhDs hired for work MS students used to do.
Reduced teaching load for research-active faculty	Necessary to pursue additional competitive grants.	Increased demand for untenured, adjunct faculty to teach classes.
"Teachers rewarded for increased student evaluation scores."	"Improved accountability; ensure customer satisfaction."	Reduced course work, grade inflation.
"Teachers rewarded for increased student test scores."	"Improve teacher effectiveness."	"Teaching to the tests; emphasis on short-term learning."
"Departments rewarded for increasing U.S. News ranking."	"Stronger departments."	Extensive efforts to reverse engineer, game, and cheat rankings.
"Departments rewarded for increasing numbers of BS, MS, and PhD degrees granted."	"Promote efficiency; stop students from being trapped in degree programs; impress the state legislature."	"Class sizes increase; entrance requirements" decrease; reduce graduation requirements.
"Departments rewarded for increasing student credit/contact hours (SCH)."	"The university's teaching mission is fulfilled."	"SCH-maximization games are played": duplication of classes, competition for service courses.

Modified from Regehr (pers. comm., 2015) with permission.

Quantitative performance metrics: effect on individual researchers and productivity.

The goal of measuring scientific productivity has given rise to quantitative performance metrics, including publication count, citations, combined citation-publication counts (e.g., h-index), journal impact factors (JIF), total research dollars, and total patents. These quantitative metrics now dominate decision-making in faculty hiring, promotion and tenure, awards, and funding (Abbott et al., 2010; Carpenter et al., 2014). Because these measures are subject to manipulation, they are doomed to become misleading and even counterproductive, according to Goodhart's Law, which states that "when a measure becomes a target, it ceases to be a good measure" (Elton, 2004; Fischer et al., 2012; Werner, 2015).

Ultimately, the well-intentioned use of quantitative metrics may create inequities and outcomes worse than the systems they replaced. Specifically, if rewards are disproportionally given to individuals manipulating their metrics, problems of the old subjective paradigms (e.g., old-boys' networks) may be tame by comparison. In a 2010 survey, 71% of respondents stated that they feared colleagues can "game" or "cheat" their way into better evaluations at their institutions (Abbott, 2010), demonstrating that scientists are acutely attuned to the possibility of abuses in the current system.

Quantitative metrics are scholar centric and reward output, which is not necessarily the same as achieving a goal of socially relevant and impactful research outcomes. Scientific output as measured by cited work has doubled every 9 years since about World War II (Bornmann and Mutz, 2015), producing "busier academics, shorter and less comprehensive papers" (Fischer et al., 2012), and a change in climate from "publish or perish" to "funding or famine" (Quake, 2009; Tijdink et al., 2014). Questions have been raised about how sustainable this exponential increase in the knowledge industry is (Price, 1963; Frodeman, 2011) and how much of the growth is illusory and results from manipulation as per Goodhart's Law.

Recent exposés have revealed schemes by journals to manipulate impact factors, use of p-hacking by researchers to mine for statistically significant and publishable results, rigging of the peer-review process itself, and overcitation (Falagas and Alexiou, 2008; Labbé, 2010; Zhivotovsky and Krutovsky, 2008; Bartneck and Kokkelmans, 2011; Delgado López-Cózar et al., 2012; McDermott, 2013; Van Noorden, 2014; Barry, 2015). A fictional character was recently created to demonstrate a "spamming war in the heart of science," by generation of 102 fake articles and a stellar h-index of 94 on Google Scholar (Labbé, 2010). Blogs describing how to more discretely raise h-index without committing outright fraud are also commonplace (e.g., Dem, 2011).

It is instructive to conceptualize the basic problem from a perspective of emphasizing quality-in-research versus quantity-in-research, as well as effects of perverse incentives (Figure 6-1). Assuming that the goal of the scientific enterprise is to maximize true

scientific progress, a process that overemphasizes quality might require triple or quadruple blinded studies, mandatory replication of results by independent parties, and peer-review of all data and statistics before publication—such a system would minimize mistakes, but would produce very few results due to overcaution (left Fig. 1). At the other extreme, an overemphasis on quantity is also problematic because accepting less scientific rigor in statistics, replication, and quality controls or a less rigorous review process would produce a very high number of articles, but after considering costly setbacks associated with a high error rate, true progress would also be low. A hypothetical optimum productivity lies somewhere in between, and it is possible that our current practices (enforced by peer review) evolved to be near the optimum in an environment with fewer perverse incentives.

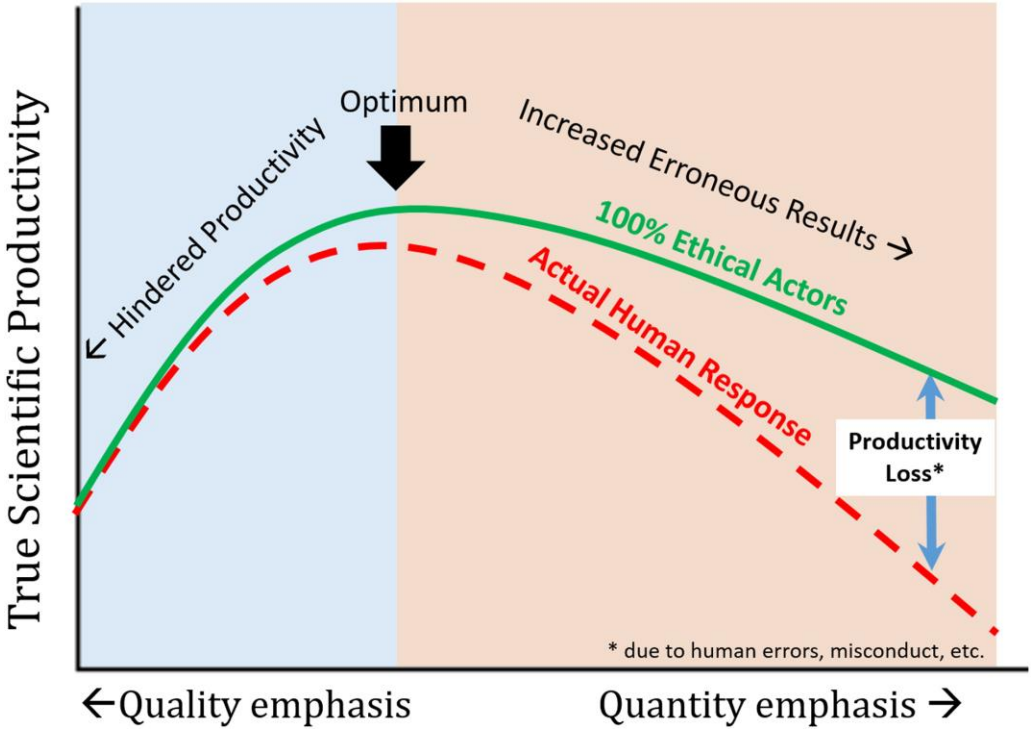

Figure 6-1. True scientific productivity vis-à-vis emphasis on research quality/quantity.

However, over the long term under a system of perverse incentives, the true productivity curve changes due to increased manipulation and/or unethical behavior (Fig. 1). In a system overemphasizing quality, there is less incentive to cut corners because checks and balances allow problems to be discovered more easily, but in a system emphasizing quantity, productivity can be dramatically reduced by massive numbers of erroneous articles created by carelessness, subtle falsification (i.e., eliminating bad data), and substandard review if not outright fabrication (i.e., dry labbing).

While there is virtually no research exploring the impact of perverse incentives on scientific productivity, most in academia would acknowledge a collective shift in our behavior over the years (Table 6-1), emphasizing quantity at the expense of quality. This

issue may be especially troubling for attracting and retaining altruistically minded students, particularly women and underrepresented minorities (WURM), in STEM research careers. Because modern scientific careers are perceived as focusing on "the individual scientist and individual achievement" rather than altruistic goals (Thoman et al., 2014), and WURM students tend to be attracted toward STEM fields for altruistic motives, including serving society and one's community (Diekman et al., 2010, Thoman et al., 2014), many leave STEM to seek careers and work that is more in keeping with their values (e.g., Diekman et al., 2010; Gibbs and Griffin, 2013; Campbell, et al., 2014).

Thus, another danger of overemphasizing output versus outcomes and quantity versus quality is creating a system that is a "perversion of natural selection," which selectively weeds out ethical and altruistic actors, while selecting for academics who are more comfortable and responsive to perverse incentives from the point of entry. Likewise, if normally ethical actors feel a need to engage in unethical behavior to maintain academic careers (Edwards, 2014), they may become complicit as per Granovetter's well-established Threshold Model of Collective Behavior (1978). At that point, unethical actions have become "embedded in the structures and processes" of a professional culture, and nearly everyone has been "induced to view corruption as permissible" (Ashforth and Anand, 2003).

It is also telling that a new genre of articles termed "quit lit" by the Chronicle of Higher Education has emerged (Chronicle Vitae, 2013–2014), in which successful, altruistic, and public-minded professors give perfectly rational reasons for leaving a profession they once loved—such individuals are easily replaced with new hires who are more comfortable with the current climate. Reasons for leaving range from a saturated job market, lack of autonomy, concerns associated with the very structure of academe (CHE, 2013), and "a perverse incentive structure that maintains the status quo, rewards mediocrity, and discourages potential high-impact interdisciplinary work" (Dunn, 2013).

Summary

While quantitative metrics provide an objective means of evaluating research productivity relative to subjective measures, now that they have become a target, they cease to be useful and may even be counterproductive. A continued overemphasis on quantitative metrics will pressure all but the most ethical scientists, to overemphasize quantity at the expense of quality, create pressures to "cut corners" throughout the system, and select for scientists attracted to perverse incentives.

Scientific societies, research institutions, academic journals and individuals have made similar arguments, and some have signed the San Francisco Declaration of Research Assessment (DORA). The DORA recognizes the need for improving "ways in which output of scientific research are evaluated" and calls for challenging research assessment practices, especially the JIF, which are currently in place. Signatories include the American Society for Cell Biology, American Association for the Advancement of Science, Howard Hughes Medical Institute, and Proceedings of The National Academy of Sciences, among 737 organizations and 12,229 individuals as of June 30, 2016. Indeed, publishers of Nature, Science, and other journals have called for downplaying the

JIF metric, and the American Society of Microbiology is announcing plans to "purge the conversation of the impact factor" and remove them from all their journals (Callaway, 2016). The argument is not to get rid of metrics, but to reduce their importance in decision-making by institutions and funding agencies, and perhaps invest resources toward creating more meaningful metrics (ACSB, 2012). DORA would be a step in the right direction of halting the "avalanche" of performance metrics dominating research assessment, which are unreliable and have long been hypothesized to threaten the quality of research (Rice, 1994; Macilwain, 2013).

Performance metrics: effect on institutions

We had to get into the top 100. That was a life-or-death matter for Northeastern. — Richard Freeland, Former President of Northeastern University (Kutner, 2014)

The perverse incentives for academic institutions are growing in scope and impact, as best exemplified by U.S. News & World Report annual rankings that purportedly measure "academic excellence" (Morse, 2015). The rankings have strongly influenced, positively or negatively, public perceptions regarding the quality of education and opportunities they offer (Casper, 1996; Gladwell, 2011; Tierney, 2013). Although U.S. News & World Report rankings have been dismissed by some, they still undeniably wield extraordinary influence on college administrators and university leadership—the perceptions created by the objective quantitative ranking determines "how students, parents, high schools, and colleges pursue and perceive education" in practice (Kutner, 2014; Segal, 2014).

The rankings rely on subjective proprietary formula and algorithms, the original validity of which has since been undermined by Goodhart's law—universities have attempted to game the system by redistributing resources or investing in areas that the ranking metrics emphasize. Northeastern University, for instance, unapologetically rose from #162 in 1996 to #42 in 2015 by explicitly changing their class sizes, acceptance rates, and even peer assessment. Others have cheated by reporting incorrect statistics (Bucknell University, Claremont-McKenna College, Clemson University, George Washington University, and Emory University are examples of those who were caught) to rise in the ranks (Slotnik and Perez-Pena, 2012; Anderson, 2013; Kutner, 2014). More than 90% of 576 college admission officers thought other institutions were submitting false data to U.S. News according to a 2013 Gallup and Inside Higher Ed poll (Jaschik, 2013), which creates further pressures to cheat throughout the system to maintain a ranking perceived to be fair as discussed in preceding sections.

Hypercompetitive funding environments

If the work you propose to do isn't virtually certain of success, then it won't get funded — Roger Kornberg, Nobel laureate (Lee, 2007)

The only people who can survive in this environment are people who are absolutely passionate about what they're doing and have the self-confidence and competitiveness to

just go back again and again and just persistently apply for funding — Robert Waterland, Baylor College of Medicine (Harris and Benincasa, 2014)

The federal government's role in financing research and development (R&D), creating new knowledge, or fulfilling public missions like national security, agriculture, infrastructure, and environmental health has become paramount. The cost of high-risk, long-term research, which often has uncertain prospects and/or utility, has been largely borne by the U.S. government in the aftermath of World War II, forming part of an ecosystem with universities and industries contributing to the collective progress of mankind (Bornmann and Mutz, 2015; Hourihan, 2015).

However, in the current competitive global environment where China is projected to outspend the U.S. on R&D by 2020, some worry that the "edifice of American innovation rests on an increasingly rickety foundation" because of a decline in spending on federal R&D in the past decade (Casassus, 2014; OECD, 2014; MIT, 2015; Porter, 2015). U.S. "Research Intensity" (i.e., federal R&D as a share of the country's gross domestic product or GDP) has declined to 0.78% (2014), which is down from about 2% in the 1960 s (Figure 6-2). With discretionary spending of federal budgets projected to decrease, research intensity is likely to drop even further, despite increased industry funding (Hourihan, 2015).

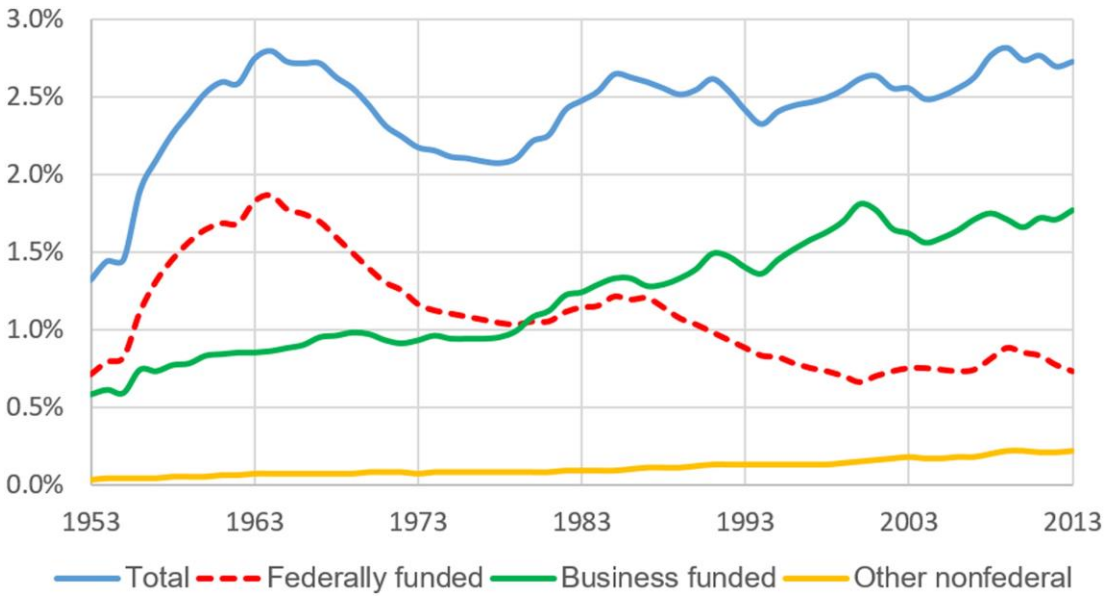

Figure 6-2. Trends in research intensity (i.e., ratio of U.S. R&D to gross domestic product), roles of federal, business, and other nonfederal funding for R&D: 1953–2013.
Data source: National Science Foundation, National Center for Science and Engineering Statistics, National Patterns of R&D Resources (annual series). R&D, research and development.

A core mission of American colleges and universities has been "service to the public," and this goal will be more difficult to reach as universities morph into profit centers

churning out patents and new products (Faust, 2009; Mirowski, 2011; Brownlee, 2014; Hinkes-Jones, 2014; Seligsohn, 2015; American Academy of Arts and Sciences, 2016). Until the late 2000s, research institutions and universities went on a building spree fueled by borrowing, with an expectation that increased research funding would allow them to further boost research productivity—a cycle that went bust after the 2007–2008 financial crash (Stephan, 2012a). Universities are also allowed to offset debt from ill-fated expansion efforts as indirect costs (Stephan, 2012b), which increases overhead and decreases dollars available to spend on research even if funds raised by grants remain constant.

The static or declining federal investment in research has created the "worst research funding <scenario in 50 years>" and further ratcheted competition for funding (Lee, 2007; Quake, 2009; Harris and Benincasa, 2014; Schneider et al., 2014; Stein, 2015), given that the number of researchers competing for grants is rising. The funding rate for NIH grants fell from 30.5% to 18% between 1997 and 2014, and the average age for a first time PI on an R01-equivalent grant has increased to 43 years (NIH, 2008, 2015). NSF funding rates have remained stagnant between 23 and 25% in the past decade (NSF, 2016). While these funding rates are still well above the breakeven point of 6%, at which the net cost of proposal writing equals the net value obtained from a grant by the grant winner (Cushman et al., 2015), there is little doubt the grant environment is hypercompetitive, susceptible to reviewer biases, and strongly dependent on prior success as measured by quantitative metrics (Lawrence, 2009; Fang and Casadevall, 2016). Researchers must tailor their thinking to align with solicited funding, and spend about half of their time addressing administrative and compliance, drawing focus away from scientific discovery and translation (NSB, 2014; Schneider et al., 2014; Belluz et al., 2016).

SYSTEMIC RISKS TO SCIENTIFIC INTEGRITY

Science is a human endeavor, and despite its obvious historical contributions to advancement of civilization, there is growing evidence that today's research publications too frequently suffer from lack of replicability, rely on biased data-sets, apply low or substandard statistical methods, fail to guard against researcher biases, and their findings are overhyped (Fanelli, 2009; Aschwanden, 2015; Belluz and Hoffman, 2015; Nuzzo, 2015; Gobry, 2016; Wilson, 2016). A troubling level of unethical activity, outright faking of peer review and retractions, has been revealed, which likely represents just a small portion of the total, given the high cost of exposing, disclosing, or acknowledging scientific misconduct (Marcus and Oransky, 2015; Retraction Watch, 2015a; BBC, 2016; Borman, 2016). Warnings of systemic problems go back to at least 1991, when NSF Director Walter E. Massey noted that the size, complexity, and increased interdisciplinary nature of research in the face of growing competition was making science and engineering "more vulnerable to falsehoods" (The New York Times, 1991).

Misconduct is not limited to academic researchers. Federal agencies are also subject to perverse incentives and hypercompetition, giving rise to a new phenomenon of institutional scientific research misconduct (Lewis, 2014; Edwards, 2016). Recent

exemplars uncovered by the first author in the Flint and Washington D.C. drinking water crises include "scientifically indefensible" reports by the U.S. Centers for Disease Control and Prevention (U.S. Centers for Disease Control and Prevention, 2004; U.S. House Committee on Science and Technology, 2010), reports based on nonexistent data published by the U.S. EPA and their consultants in industry journals (Reiber and Dufresne, 2006; Boyd et al., 2012; Edwards, 2012; Retraction Watch, 2015b; U.S. Congress House Committee on Oversight and Government Reform, 2016), and silencing of whistleblowers in EPA (Coleman-Adebayo, 2011; Lewis, 2014; U.S. Congress House Committee on Oversight and Government Reform, 2015). This problem is likely to increase as agencies increasingly compete with each other for reduced discretionary funding. It also raises legitimate and disturbing questions as to whether accepting research funding from federal agencies is inherently ethical or not—modern agencies clearly have conflicts similar to those that are accepted and well understood for industry research sponsors. Given the mistaken presumption of research neutrality by federal funding agencies (Oreskes and Conway, 2010), the dangers of institutional research misconduct to society may outweigh those of industry-sponsored research (Edwards, 2014).

A "trampling of the scientific ethos" witnessed in areas as diverse as climate science and galvanic corrosion undermines the "credibility of everyone in science" (Bedeian et al., 2010; Oreskes and Conway, 2010; Edwards, 2012; Leiserowitz et al., 2012; The Economist, 2013; BBC, 2016). The Economist recently highlighted the prevalence of shoddy and nonreproducible modern scientific research and its high financial cost to society—posing an open question as to whether modern science was trustworthy, while calling upon science to reform itself (The Economist, 2013). And, while there are hopes that some problems could be reduced by practices that include open data, open access, postpublication peer review, metastudies, and efforts to reproduce landmark studies, these can only partly compensate for the high error rates in modern science arising from individual and institutional perverse incentives (Fig. 1).

The high costs of research misconduct

The National Science Foundation defines research misconduct as intentional "fabrication, falsification, or plagiarism in proposing, performing, or reviewing research, or in reporting research results" (Steneck, 2007; Fischer, 2011). Nationally, the percentage of guilty respondents in research misconduct cases investigated by the Department of Health and Human Services (includes NIH) and NSF ranges from 20% to 33% (U.S. Department of Health and Human Services, 2013; Kroll, 2015, pers. comm.). Direct costs of handling each research misconduct case are $525,000, and over $110 million are incurred annually for all such cases at the institutional level in the U.S (Michalek, et al., 2010). A total of 291 articles retracted due to misconduct during 1992–2012 accounted for $58 M in direct funding from the NIH, which is less than 1% of the agency's budget during this period, but each retracted article accounted for about $400,000 in direct costs (Stern et al., 2014).

Obviously, incidence of undetected misconduct is some multiple of the cases judged as such each year, and the true incidence is difficult to predict. A comprehensive meta-

analysis of research misconduct surveys between 1987 and 2008 indicated that 1 in 50 scientists admitted to committing misconduct (fabrication, falsification, and/or modifying data) at least once and 14% knew of colleagues who had done so (Fanelli, 2009). These numbers are likely an underestimate considering the sensitivity of the questions asked, low response rates, and the Muhammad Ali effect (a self-serving bias where people perceive themselves as more honest than their peers) (Allison et al., 1989). Indeed, delving deeper, up to 34% of researchers self-reported that they have engaged in "questionable research practices," including "dropping data points on a gut feeling" and "changing the design, methodology, and results of a study in response to pressures from a funding source," whereas up to 72% of those surveyed knew of colleagues who had done so (Fanelli, 2009). One study included in Fanelli's meta-analysis looked at rates of exposure to misconduct for 2,000 doctoral students and 2,000 faculty from the 99 largest graduate departments of chemistry, civil engineering, microbiology, and sociology, and found between 6 and 8% of both students and faculty had direct knowledge of faculty falsifying data (Swazey et al., 1993).

In life science and biomedical research, the percentage of scientific articles retracted has increased 10-fold since 1975, and 67% were due to misconduct (Fang et al., 2012). Various hypotheses are proposed for this increase, including "lure of the luxury journal," "pathological publishing," prevalent misconduct policies, academic culture, career stage, and perverse incentives (Martinson et al., 2009; Harding et al., 2012; Laduke, 2013; Schekman, 2013; Buela-Casal, 2014; Fanelli et al., 2015; Marcus and Oransky, 2015; Sarewitz, 2016). Nature recently declared that "pretending research misconduct does not happen is no longer an option" (Nature, 2015).

Academia and science are expected to be self-policing and self-correcting. However, based on our experiences, we believe there are incentives throughout the system that induce all stakeholders to "pretend misconduct does not happen." Science has never developed a clear system for reporting, investigating, or dealing with allegations of research misconduct, and those individuals who do attempt to police behavior are likely to be frustrated and suffer severe negative professional repercussions (Macilwain, 1997; Kevles, 2000; Denworth, 2008). Academics largely operate on an unenforceable and unwritten honor system, in relation to what is considered fair in reporting research, grant writing practices, and "selling" research ideas, and there is serious doubt as to whether science as a whole can actually be considered self-correcting (Stroebe et al., 2012). While there are exceptional cases where individuals have provided a reality check on overhyped research press releases in areas deemed potentially transformative (e.g., Eisen, 2010–2015; New Scientist, 2016), limitations of hot research sectors are more often downplayed or ignored. Because every modern scientific mania also creates a quantitative metric windfall for participants and there are few consequences for those responsible after a science bubble finally pops, the only true check on pathological science and a misallocation of resources is the unwritten honor system (Langmuir et al., 1953).

If nothing is done, we will create a corrupt academic culture

The modern academic research enterprise, dubbed a "Ponzi Scheme" by The Economist, created the existing perverse incentive system, which would have been almost inconceivable to academics of 30–50 years ago (The Economist, 2010). We believe that this creation is a threat to the future of science, and unless immediate action is taken, we run the risk of "normalization of corruption" (Ashforth and Anand, 2003), creating a corrupt professional culture akin to that recently revealed in professional cycling or in the Atlanta school cheating scandal.

To review, for the 7 years Lance Armstrong won the Tour de France (1999–2005), 20 out of 21 podium finishers (including Armstrong) were directly tied to doping through admissions, sanctions, public investigations, or failing blood tests. Entire teams cheated together because of a "win-at-all cost culture" that was created and sustained over time because there was no alternative in sight (U.S. ADA, 2012; Rose and Fisher, 2013; Saraceno, 2013). Numerous warning signs were ignored, and a retrospective analysis indicates that more than half of all Tour de France winners since 1980 had either been tested positive for or confessed to doping (Mulvey, 2012). The resultant "culture of doping" put clean athletes under suspicion (CIRC, 2015; Dimeo, 2015) and ultimately brought worldwide disrepute to the sport.

Likewise, the Atlanta Public Schools (APS) scandal provides another example of a perverse incentive system run to its logical conclusion, but in an educational setting. Twelve former APS employees were sent to prison and dozens faced ethics sanctions for falsifying students' results on state-standardized tests. The well-intentioned quantitative test results became high stakes to the APS employees, because the law "trigger[s] serious consequences for students (like grade promotion and graduation); schools (extra resources, reorganization, or closure); districts (potential loss of federal funds), and school employees (bonuses, demotion, poor evaluations, or firing)" (Kamenetz, 2015). The APS employees betrayed their stated mission of creating a "caring culture of trust and collaboration [where] every student will graduate ready for college and career," and participated in creating the illusion of a "high-performing school district" (APS, 2016). Clearly, perverse incentives can encourage unethical behavior to manipulate quantitative metrics, even in an institution where the sole goal was to educate children.

An uncontrolled perverse incentive system can create a climate in which participants feel they must cheat to compete, whether it is academia (individual or institutional level) or professional sports. While procycling was ultimately discredited and its rewards were not properly distributed to ethical participants, in science, the loss of altruistic actors and trust, and risk of direct harm to the public and the planet raise the dangers immeasurably.

WHAT KIND OF PROFESSION ARE WE CREATING FOR THE NEXT GENERATION OF ACADEMICS?

So I have just one wish for you—the good luck to be somewhere where you are free to maintain the kind of integrity I have described, and where you do not feel forced by a need to maintain your position in the organization, or financial support, or so on, to lose your integrity. May you have that freedom — Richard Feynman, Nobel laureate (Feynman, 1974)

The culture of academia has undergone dramatic change in the last few decades—quite a bit of it has been for the better. Problems with diversity, work-life balance, funding, efficient teaching, public outreach, and engagement have been recognized and partly addressed.

As stewards of the profession, we should continually consider whether our collective actions will leave our field in a state that is better or worse than when we entered it. While factors such as state and federal funding levels are largely beyond our control, we are not powerless and passive actors. Problems with perverse incentives and hypercompetition could be addressed by the following:

1) The scope of the problem must be better understood, by systematically mining the experiences and perceptions held by academics in STEM fields, through a comprehensive survey of high-achieving graduate students and researchers.

2) The National Science Foundation should commission a panel of economists and social scientists with expertise in perverse incentives, to collect and review input from all levels of academia, including retired National Academy members and distinguished STEM scholars. The panel could also develop a list of "best practices" to guide evaluation of candidates for hiring and promotion, from a long-term perspective of promoting science in the public interest and for the public good, and maintain academia as a desirable career path for altruistic ethical actors.

3) Rather than pretending that the problem of research misconduct does not exist, science and engineering students should receive instruction on these subjects at both the undergraduate and graduate levels. Instruction should include a review of real world pressures, incentives, and stresses that can increase the likelihood of research misconduct.

4) Beyond conventional goals of achieving quantitative metrics, a PhD program should also be viewed as an exercise in building character, with some emphasis on the ideal of practicing science as service to humanity (Huber, 2014).

5) Universities need to reduce perverse incentives and uphold research misconduct policies that discourage unethical behavior.

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CHAPTER 6. HIJACKING OF CITIZEN SCIENCE BY CITIZEN ENGINEERS: LESSONS IN SCIENCE ANARCHY FROM THE FLINT WATER CRISIS

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ABSTRACT

A citizen science collaboration between Flint residents, the Virginia Tech "Flint Water Study" team, and other groups helped uncover the Flint Lead-in-Drinking Water Crisis and Legionella outbreaks in large multi-story buildings. Those findings contributed to a Federal Emergency declaration in January 2016, hundreds of millions of dollars in relief funding, a widely acknowledged revelation of an environmental injustice, and resignations or indictments for some responsible public officials. Following this triumph, after responsible government agencies had rededicated themselves to making amends and helping the recovery, Flint became a high profile battlefield between citizen scientists and their government agency collaborators, and practitioners of "citizen engineering." Citizen engineers are dedicated to "undermine engineering <and science> expertise" in the name of "democratizing" science. Because citizen engineers do not aspire to either rigor or objectivity, they define themselves by biases and conflicts of interest that true scientists aspire to guard against. Representative problems attributed to citizen engineering in Flint included: 1) collection of non-representative data that created un-necessary fear amongst residents about the safety of water used for bathing and showering, 2) failure to disclose obvious financial conflicts of interest, and 3) misrepresentation or falsification of data to obtain relief resources, support lawsuits, or scientific hypotheses known to be false. "Citizen engineering" is an aspiration to "science anarchy" by definition, and our documented experiences highlight its dangers to future citizen science endeavors.

KEYWORDS: Citizen Science, Citizen Engineering, Flint Water Crisis, Misconduct, Conflicts of Interest, Science Communication, Disinfection Byproducts, Shigella

INTRODUCTION: ORIGINS OF A WATER CRISIS

In an effort to save about 5 million dollars while a new water pipeline was being built, Michigan state-appointed Emergency Managers switched drinking water sources for the City of Flint from Lake Huron [purchased from the Detroit Water and Sewerage Department (DWSD)] to the local Flint River on April 25, 2014 (Fonger, 2015). A failure to install federally mandated corrosion control treatment, unleashed a "perfect storm" within Flint's antiquated water distribution system comprised of unlined iron water mains, lead/galvanized steel service pipes and lead-bearing internal plumbing. The uncontrolled corrosion rapidly depleted the chlorine disinfectant residual in the system, allowed elevated levels of microbes including *Escherichia coli* and *Legionella pneumophila*. An in-depth scientific analysis of deficiencies that caused Flint's water quality problems can be found elsewhere (Schwake et al. 2016; Allen et al. 2017; Olson et al. 2017; Pieper, Tang & Edwards 2017; Rhoads et al. 2017).

In parallel with these scientific and engineering problems, there was a well-deserved loss of public trust due to the documented failures of government agencies at multiple levels (Bernstein and Dennis 2016, Canepari and Leduff 2016; Edwards 2016a; Edwards 2016b). Analysis of Google web searches illustrates that Flint residents began unusual online search activity for information about their tap water soon after the switch in Summer 2014 (Matsa, Mitchell & Stocking 2017). A series of red flags indicating growing problems were reported by consumers to appropriate local and state government officials during the time period in which Flint River water was being used (Apr 2014-Oct 2015), and all of these warnings were either ignored or covered up (Edwards 2016). Obvious problems included reports of red water, hair loss and skin rashes, three boil water advisories, General Motors noticing the Flint water was causing rusting of their engine parts, and exceedances of disinfection byproduct regulations. But the crisis entered a new phase when high lead levels (> 100 ppb) were detected by a City of Flint official in the home of LeeAnne Walters (Pieper, Tang & Edwards 2017).

UNCOVERING THE FLINT WATER CRISIS WITH CITIZEN SCIENCE

"We proved that citizens and scientists working together could form a great alliance, and that grass-roots science can have a sky-high impact" – LeeAnne Walters (Flint Water Study 2016)

After Walters' (aka "Resident Zero") discovery of high lead in her home, she sought to became a truth-seeking citizen scientist, who systematically educated herself about water lead issues, diagnosed elevated blood lead in her children, began collaborating with one of the foremost national experts on the federal Lead and Copper Rule (LCR) at the US Environmental Protection Agency (EPA), and was instrumental in helping to prove there was no lead corrosion control in the City's water (Lurie 2016; Smith and Thomson 2017). In April 2015, Walters sampled her water with the scientists who eventually became the Flint Water Study citizen science team ("Virginia Tech"), demonstrating hazardous waste levels of water lead in her water even after prolonged flushing (Pieper, Tang & Edwards 2017). That discovery and data, in turn, contributed to a detailed technical memo by the

EPA expert highlighting an imminent and substantial endangerment to Flint residents in late June 2015 (Del Toral 2015). Rather than acting on this information, in early August 2015, Walters and other residents learned that the Michigan Department of Environmental Quality (MDEQ) who has primacy responsibility for safety of Flint water, planned to cover up these problems without any protest from EPA (Roy and Edwards 2015; EPA OIG 2016).

An unprecedented citizen science collaboration was then organized by Virginia Tech, American Civil Liberties Union-Michigan, activist groups, Walters and many other Flint residents in early Aug 2015. Virginia Tech provided the technical plan, analytical support and funding, while Flint residents donated their local knowledge, homes as test sites, and sweat equity in coordinating and executing sampling plans. The collaboration started with a team from Virginia Tech sampling the water distribution system, water heaters and home plumbing for a wide array of potential chemical and microbial contaminants, which later expanded to a citizen coordinated citywide sampling event focused on water lead that ultimately involved 269 Flint homes geographically distributed across the city. Of the hundreds of analytes examined in the initial phase of testing summer 2015 by the Virginia Tech team, only lead was determined likely to exceed federal LCR standards (Edwards 2015; Cooper 2016; Paynter 2016; Averett 2017; Rhoads et al. 2017). That result, coupled to later independent analysis demonstrating rising blood lead in some Flint children by researchers at Hurley Medical Center, led local medical authorities and eventually the State of Michigan to acknowledge the danger (Hanna-Attisha et al. 2016). A switch back to Lake Huron water from DWSD occurred on Oct 15, 2015 and detection of Legionella at high levels in large buildings by Virginia Tech occurred in late 2015 (Rhoads et al. 2017). The latter revelation was eventually followed by an acknowledgement of a two year Legionella outbreak with about a dozen deaths, after which President Barack Obama declared a federal emergency January 13, 2016 (Wakefield 2016). The presidential declaration and associated publicity created an international media sensation, which eventually resulted in hundreds of millions of dollars of federal, state and private relief funding for Flint through the present day (French 2016).

After declaration of the Federal Emergency, the responsible and largely discredited government agencies, publicly re-dedicated themselves to the relief effort along with assistance from the Federal Emergency Management Agency (FEMA) and National Guard who distributed filters and bottled water (Wakefield 2016). The governor apologized publicly and set up a task force that included members of the Virginia Tech, Hurley, and other vocal critics to co-advise on the recovery (Bosman and Smith 2016; Johnson 2016). EPA, MDEQ and the City of Flint took additional measures to enhance disinfection and corrosion control beyond that present in water purchased from DWSD, in order to hasten the recovery of the distribution system for both microbial and chemical concerns. Subsequent citizen science sampling events tracked the water system recovery in four citizen led sampling campaigns in March 2016, July 2016, November 2016, and August 2017. Because the citizen science team, had also revealed that all prior state and city lead data was collected using so-called “cheats” to minimize lead measured at the tap – the citizen science datasets collected without cheats represented the only internally

consistent measures of lead levels during the water crisis and its aftermath. As a result the citizen and Virginia Tech sampling was federally funded throughout 2016 (Roy and Edwards 2015; Milman and Glenza 2016; Pieper, Tang & Edwards 2017; Tang et al. 2017).

These citizen science sampling events demonstrated consistent but slow improvements in tap water quality, including lead and other chemical contaminants, microbial contaminants including Legionella, and metals that cause discolored water. Regulatory monitoring by MDEQ showed no problems with disinfection by-product regulations at any point of 2016, and 90%'ile lead levels below the EPA action level since summer 2016. By summer of the 2017, the latter official measurements were no longer in significant disagreement with the citizen science monitoring data (Allen et al. 2017; Lynch and Chambers 2017; Tang et al. 2017). Fifteen civil servants within State of Michigan (including MDEQ) and City of Flint have been criminally charged for their role in the crisis (Egan 2017a).

From a scientific and regulatory standpoint, by summer 2017 Flint's water met all existing federal standards, which by some definitions could mark an end to the water crisis. But the problem of lost trust remained as "the biggest issue," which could itself be considered a crisis (Canepari and Leduff 2016; Adewunmi 2017; Fonger 2017a). While much of the lost trust in government science was self-inflicted and deserved through at least early 2016, we will also argue herein that the real progress of the relief effort after that time, was systematically undermined by unscrupulous and unethical "citizen engineers" in the guise of citizen scientists.

CITIZEN ENGINEERING AS SCIENCE ANARCHY

Riley and colleagues (2016) define "citizen engineering" as an exercise by which:

> "community members ("non-experts") identify scientific questions and proceed through a formal process…sometimes but not always with the cooperation of trained scientists," with "…the disruption of engineering expertise is a central goal…."

This philosophy was later expanded to getting rid of the concept of "rigor" entirely in science and engineering "so we can welcome other ways of knowing (Riley 2017a)," and thereby eliminate "the profession's tendency to marginalize, ignore, silence,…<l>ocal knowledges and scientific counter-knowledges that depart from dominant paradigms of engineering thought and practice (Riley and Lambrinidou 2015)."

The work of Riley and colleagues (2015, 2016, 2017a) embody a logical evolution of postmodern science (Kuntz 2012) to engineering. Kuntz warned that "the danger of a postmodern approach to science, that seeks to include all points of view as equally valid, is that it slows down and prevents much needed scientific research, even denying that science should have a role in such decisions." He further notes that postmodernists attempt to replace "apolitical scientists, especially for risk assessment, with "experts"

sympathetic to the cause; …irrespective of whether their opinion is accepted by other scientists or whether their research and conclusions are trustworthy," and that the resulting "assault" on science "comes disguised in the clothes of democracy, freedom of speech and tolerance of opinion (Kuntz 2012)."

Given that anarchy is defined by an absence of established order, "citizen engineering" with an explicit goal of "disrupting engineering expertise," is a form of "science anarchy" and its practitioners are properly termed "science anarchists." As this case study will demonstrate, the fact that "citizen engineers," repeatedly and irresponsibly attacked expertise of government science agencies and others during the Flint water crisis relief effort, and endangered the public welfare in the process, makes use of these terms especially appropriate.

WATER DEFENSE'S "CITIZEN SCIENCE" PROGRAM IN FLINT COINCIDES WITH SHARP SPIKE IN SHIGELLOSIS CASES

"[We shouldn't be having the debate of] whether or not my organization [Water Defense] is (sic) scientists, because we are admitting we are citizen scientists. ...All we are doing is giving people information and there is nothing wrong with that. And the more information people have, the better off they are" – Mark Ruffalo (Water Defense 2016a)

Unscientific WaterBug® testing and conflicts of interest

"George Orwell first noted, the true genius in advertising is to sell you the solution and the problem." ― Ben Goldacre, Bad Science (Goldacre 2011)

Scott Smith, appointed "Chief Scientist" of actor Mark Ruffalo's environmental nonprofit Water Defense, came to Flint in late-January 2016, months after the switch back to Detroit water and just two weeks after President Obama's declaration of a Federal emergency which mobilized FEMA and the national guard (Delaney 2016a; Wakefield 2016; Water Defense 2016b; Roy 2017). Mr. Smith and Water Defense had recently launched WaterBug® - a green tentacled sponge product designed to "empower citizens to take water quality testing into their own hands and protect themselves (Ruffalo 2015)."

Over the next 5 months, investigations by our team and others, revealed that Mr. Smith (a self-identified entrepreneur) had no formal scientific credentials, as well as numerous undisclosed financial conflicts of interest especially considering a high profile public role with a 501(c)(3) nonprofit operating in a Federal Emergency situation. As the inventor of the foam materials used in the WaterBug®, Mr. Smith received royalty payments from the manufacturer for their purchase (Delaney 2016a). In May 2016, Mr. Smith also launched a for-profit company, Aquaflex™, which we showed was pitched to investors as a maker of proprietary filtration systems to "satisfy unmet needs" as the Water Defense non-profit "continue<d> to identify and diagnose water contamination sites." While Mr. Smith publicly asserted at a Water Defense press conference in March 2016 that "The ultimate solution here is…to create green jobs, to create…solar powered [water] filtration [systems]…and help the economy in the process," he never mentioned

his financial conflicts or personal vision to sell the filters himself through his private Aquaflex™ side venture (OPFLEXInventor 2013; Business Wire 2016; Delaney 2016a; Edwards 2016c; Justice League NYC 2016).

Citizen science sampling efforts must be rigorous and defensible, and whenever possible use established protocols (e.g., from *Standard Methods for the Examination of Water and Wastewater*, 23rd ed.; APHA, AWWA and WEF 2017). They must also try to practice appropriate quality assurance/quality control, maintain data integrity, and provide proper controls when appropriate to compare results to other geographic locations or federal standards (e.g., from the U.S. EPA and WHO). For example, proper lead-in-water testing requires collecting 1L water samples from the cold water kitchen or bathroom tap after a minimum 6 hr stagnation time according to EPA regulations (Pieper, Tang and Edwards 2017). In contrast, the proprietary Water Defense WaterBug® had never been compared or calibrated against any accepted water testing standard, subject to any peer-review, or even product tested by standards organizations such as the National Sanitation Foundation. It eventually became apparent that the floating WaterBug® sponges (less than 10% submerged in water) absorbed chemicals from both water and ambient air, creating confusion when captured contaminants were assumed to come from the water (Virginia Tech 2016; Williams 2016). Not surprisingly this deficiency created problems. At one point, Mr. Smith discouraged a Flint resident from bathing and showering because the WaterBug® detected high levels of acetone, which set off a frantic search for sources of acetone contamination to the water supply—the resident later determined on her own, that her bathroom contained multiple bottles of nail polish remover (100% acetone) which likely caused the false positive initially attributed to water (K. Webber, personal communication, Feb 4 2018).

During Jan-May 2016, Water Defense also routinely collected water samples in Flint homes from non-regulatory and improper sources including hose bibs, water meters, water heaters, and sediment clean out valves. All of these improper sampling locations create well-known false positives for lead, due to infrequently used plumbing components that are not designed to dispense water fit for human consumption due to high lead risks (Edwards 2016d; Roy and Edwards 2017). But these high lead data were reported to residents as indicating serious health concerns. The lead data was complemented by the WaterBug® test results in "detailed lab reports" with as much as 97 pages of raw data, listing hundreds of chemicals allegedly contaminating the water, without context or reference values that would allow residents to judge what was normal (TYT 2017a). They published press releases on their website with sensational titles: "Dangerous chemicals discovered in baths/showers of Flint, MI", held town halls and press conferences, posted on social media with the hashtag #citizenscience, and were featured prominently in local media (Emery 2016; Lynch and Carah 2016; Smith 2016a; Smith 2016b; Water Defense 2016c; Water Defense 2016d; WNEM 2016; Roy and Edwards 2017) and on Facebook groups by citizens. From their very first video, taken before they had collected or analyzed a single Flint water sample, Water Defense's made clear a bias towards finding data indicating that the water was "not safe for bathing and showering (Water Defense 2016b)." These messages, amplified on social media, started reaching Flint residents broadly during Feb-Apr 2016. For example, a TV news report

declared on March 21, 2016 that "[Mr. Smith] for weeks has been urging people in Flint not to bath (sic) in <the water> (Parkinson 2016)."

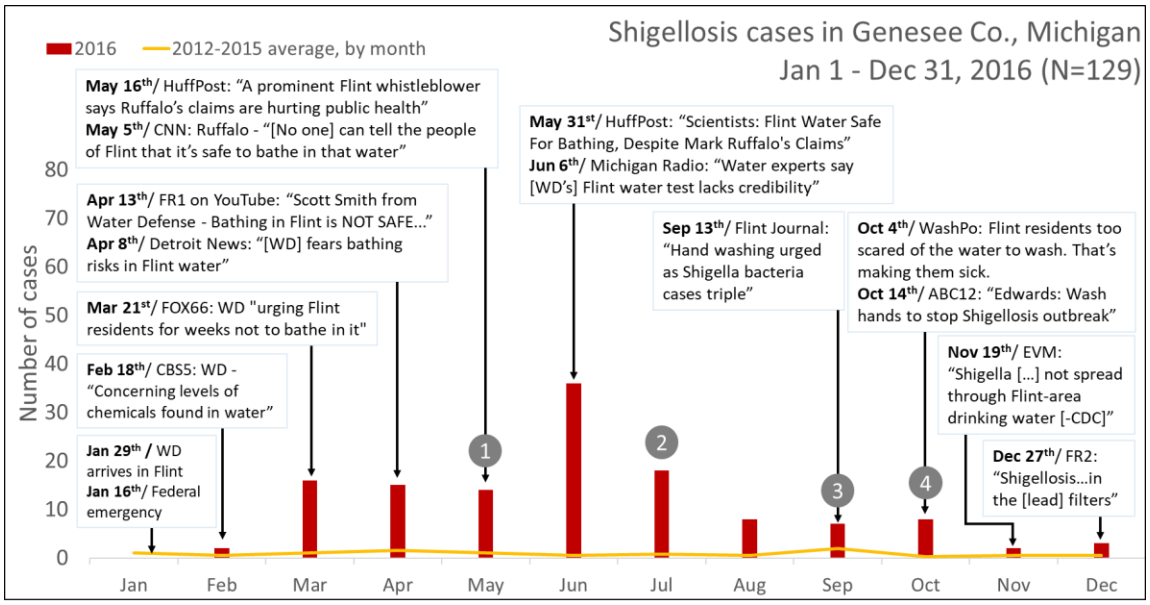
The fact that Mr. Smith had no professional degrees in science or engineering (Edwards 2016c), did not impede broadcasting his messages, and with Mr. Ruffalo's star power the lack of expertise may have even helped. Smith routinely compared himself to a budding un-credentialed Thomas Edison and Steve Jobs, and after Virginia Tech pointed out a lack of scientific credentials, his title was simply changed to "Chief Technology Officer and Investigator (OPFLEXInventor 2013; Delaney 2016a; Smith 2016c; Smith 2017)." Mr. Ruffalo, the actor, personally appeared on CNN and repeated Smith's false claims that disinfection by-products (DBPs) could be coming from Flint's pipes damaged by corrosion, and reiterated his organization's opinion that "[no one] can tell the people of Flint that it's safe to bathe in [Flint] water," directly contradicting a unified message from all the relief agencies that the Flint water at that time was not any more dangerous for bathing than other cities (CNN 2016; MDHHS 2016; Williams 2016). A Stanford professor was recruited by responsible media to flatly contradict Ruffalo's false statement about DBPs originating from pipes, supporting Virginia Tech's assertions, with some limited practical effect (Johnson 2016).

Water Defense Messaging on Bathing and Showering and Shigellosis cases in Flint

The government agencies, whose earlier claims about water safety for lead and legionella had been proven wrong by our citizen science collaboration, had little credibility in Flint at the time (Bernstein and Dennis 2016). In fact, after the unambiguous citizen science success, almost any group directly contradicting the agencies were given media coverage, with direct analogies drawn to the triumphant vindication of our citizen science team, and the agencies were loath to contradict anyone undermining scientific authority. Distrust, fear and anxiety towards the water by citizens was already justified, and residents continued to report skin rashes, hair loss, and other dermal ailments that they attributed to the water (Goodnough 2016; Roy 2017). The CDC found normal rates of these problems in Flint compared to other cities in the aftermath of the crises, but higher rates than normal during the water crisis in 2014-2015 confirming the earlier concerns of residents (CDC 2016a). During this time we personally received at least a dozen phone calls from worried residents, who cited Water Defense data and press releases, as justification for deciding to not allow families or children who were not experiencing problems, to stop taking normal baths or showers.

Perhaps not coincidentally, an outbreak of Shigellosis began (Acosta 2016; CDC 2016b) soon after Water Defense arrived in Flint (Figure 7-1). Shigellosis is a gastrointestinal illness caused by Shigella bacteria, often resulting in severe diarrhea, stomach cramps and fever. The bacteria spreads primarily through the fecal-oral pathway (i.e., by coming in contact with infected stool, soiled diapers, etc.) and only rarely from contaminated water. The disease is best controlled by normal bathing/showering and regular handwashing with soap in disinfected water (CDC 2018). Genesee Co. (where Flint is located) had a shigella incidence 35% lower than the national average when the city was being served by Flint River water during the crisis (Apr 2014-Oct 2015), which was

slightly higher than the 70% lower than national incidence rate in a comparable control period (Apr 2012-Oct 2013) before the water switch from DSWD (one-tailed paired t-test; $p < 0.05$). But shigellosis rose to 6.7 times the national incidence rate after Water Defense's arrival. It is enlightening to highlight monthly shigellosis incidence in 2016 versus public statements from Water Defense, Virginia Tech, health agencies (Genesee Co. Health Dept. or GCHD and Centers for Disease Control and Prevention or CDC) and some Flint residents during the outbreak (Figure 7-1*)*.



Shigella data courtesy: Michigan Department of Health and Human Services | ❶,❷,❸, and ❹ refer to Genesee County Health Dept. Shigella press releases on May 10th, Jul 7th, Sep 12th and Oct 7th respectively. | Acronyms: EVM = East Village Magazine, FR1 and FR2 are Flint residents, WD = Water Defense

Figure 7-1. Shigellosis cases in Flint (2012-15 v/s 2016) vis-à-vis public statements by Water Defense and other agencies on bathing, showering and shigella made on local, national or social media

References (chronological as per graph): Wakefield 2016; Water Defense 2016b; WNEM 2016; Parkinson 2016; Lynch and Carah 2016; Mays 2016a; CNN 2016; Delaney 2016b; Delaney 2016a; Williams 2016; Acosta 2016; Andrews 2016; ABC12 2016; Worth-Nelson 2016; TYT 2016a

What was the source of the outbreak? All water samples (150 total) collected by Virginia Tech from 30 Flint homes in Jun-2016, which was the peak month of the shigellosis outbreak, were later found to be negative for Shigella, inconsistent with a hypothesis of Water Defense and others that the outbreak was coming from contaminated potable water (Strom et al. 2016). . A CDC-led study relying on survey questions, clinical dermatologic evaluations and water quality testing in Flint homes (n=390) also concluded that shigella very likely did not spread through Flint-area drinking water. More likely, the misinformation on bathing and showering dangers, compounding legitimate fears of Flint residents, altered bathing habits in an adverse manner contributing to increased likelihood of shigella. In August 2016, CDC confirmed that nearly 80% of Flint residents surveyed had indeed changed their bathing and showering habits, including "showering less frequently" (75.3%), "taking shorter showers" (70.6%), and bathing in bottled or filtered

water (CDC 2016a). Of the residents in Flint that had shigellosis (n=24), 52% reported that they had changing their bathing and showering habits, much higher than other households in Genesee and Saginaw Counties (J. Yoder, Personal Communication, Feb 1 2018). The top motivating factors for these behavior changes were "media reports" and "health concerns" about bathing (CDC 2016a; CDC 2016b).

In light of Water Defense's lack of expertise and the possible public health harm arising from their problematic messaging, one of us (MAE) attempted to privately reason with the group in April 2016, well before the above studies were done indicating the source was not likely from water and altered bathing habits. Without explanation they did not participate in a scheduled teleconference meeting. They were then asked to either produce scientific evidence to back up numerous false scientific statements and publicly issue retractions, and were reminded, in no uncertain terms, of the enormous public health harm that could result if residents bathing habits were altered. Water Defense's failure to do either, made us feel ethically obligated to publicly confront what we considered to be pseudo-science on our website and harshly rebuke their irresponsible actions (Edwards 2016c; Edwards 2016d; Edwards and Roy 2016). This confrontation, which was truly a case of a citizen science team in direct conflict with a citizen engineering team, was covered in the national media and even the New York Times Magazine (Delaney 2016a; Delaney 2016b; Hohn 2016; Jerome 2016; Lynch 2016; Williams 2016).

To further combat the misinformation, we coordinated sampling events, funded by EPA, for DBPs in cold, hot and shower water in Flint households, sought written scientific opinions and analytical reports from third-party academic water experts, and assisted journalistic investigations into Mr. Smith's financial dealings (Allen et al. 2017; Delaney 2016a; Johnson 2016; Lynch 2016; Williams 2016; Roy 2017). Those efforts debunked some claims and compromised Water Defense's reputation, but hardened loyalty to Water Defense amongst some activists who were drawn to the science anarchy model in the saturation media coverage of the Flint recovery.

While a direct a cause and effect relationship cannot be proven, there is indeed a strong temporal link consistent with the conventional hypothesis regarding spread of Shigella (Figure 7-1). And at a minimum, Water Defense was sending the wrong message at the wrong time and in the wrong place, under a banner of social justice and "other ways of knowing," achieving a goal of undermining expertise of the relief agencies and other experts (Riley and Lambrinidou 2015; Riley 2017a).

During Jan-Jun 2017, only 7 shigellosis cases were reported, indicating that the risk had returned to levels considered normal. A few citizens, however, still repeat false Water Defense statements to reporters and on social media, demonstrating the staying power of bad science, not unlike the "vaccines cause autism" phenomenon.

COLLABORATION BETWEEN WATER DEFENSE AND THE LARGEST ONLINE NEWS NETWORK IN THE WORLD

"Unfortunately, the media have trouble distinguishing between real science and propaganda cross-dressed as science." -- Linda Bowles, columnist (Harmon 2000)

In Dec 2016, a politics reporter named Jordan Chariton from The Young Turks Network (TYT Politics) began work in East Chicago, IN to cover the West Calumet complex debacle – a community built atop a Superfund site grappling with serious lead-in-soil and lead-in-water contamination issues. Advised closely by Mr. Smith who was nearby working in Flint, Mr. Chariton carried out "water testing" in one home's basement by scraping the rust buildup on the outside of a basement sewer pipe for "bacterial fungi," and collecting water in an unsanitary plastic bottle from a water sediment clean out tap on a water heater (TYT 2016b).[1] The Chariton-Smith duo followed this up with testing in at least three other East Chicago homes using the WaterBug® sponge methodology and other methods they claimed were EPA approved, while recording video interviews with residents about worrisome test results that were widely disseminated via YouTube and Facebook (Roy and Edwards 2017; TYT 2017b; TYT 2017c).

Mr. Chariton repeated this type of work in Flint between Dec 2016-Oct 2017 by holding interviews, a Town Hall meeting, and uploading videos questioning Flint's improving water quality based on hearsay, statements from few Flint residents (***Section 7***), and more of Mr. Smith's flawed WaterBug® data (TYT 2016a; TYT 2016c; TYT 2017a; TYT 2017d). Mr. Smith called out traditional Flint and national journalists online as practicing "contrived reporting", characterizing multiple sources of evidence that water quality was improving as "fake news," and accusing other media as being sellouts (Roy and Edwards 2017). Chariton and Smith also pushed a conspiracy theory that the Virginia Tech citizen science team was no longer being truthful because we openly disclosed funding from the EPA and State of Michigan, and had "sold out" residents, including biased reporting of a completely innocuous recording of our conversation with a Flint resident that they edited for their prime time news (Smith 2016d; TYT 2017a). Chariton also attacked the EPA and State of MI repeatedly on air (Chariton 2017; TYT 2016d; TYT 2017e; TYT 2017f).

In collaboration with some Flint residents, we again made a difficult decision to directly undermine their messaging, which we deemed both harmful, false, and dangerous to the public welfare. To achieve that objective, we compiled vignettes from their published YouTube videos to highlight obvious improper water sampling methods (described above and in ***Section 5***) in an online blog post (Roy and Edwards 2017). The videos documented invalid methods, improper sampling locations, unsterile protocols for bacteria sampling, misrepresentation of test results – in essence, proving the complete lack of rigor, scientific understanding or established methods advocated by "citizen engineers (Riley et al. 2016; Riley 2017a)." After it aired, Mr. Chariton threatened us through a series of emails demanding we remove the blog posting or face a "public

[1] Sediment build-up is a function of source water, treated water chemistry, hardness and corrosion byproducts, is common in water heaters across the country, and not representative of the water at drinking taps.

dispute with the largest online news channel in the world," which would include future feature stories that "prove [Dr. Edwards is] a hack (Edwards and Roy 2017a)." We did not delete the videos and were indeed attacked continually online by Chariton, until he was finally fired in Nov 2017 due to a sex scandal in Flint involving an orgy with a subordinate (Lima 2017).

COLLABORATION BETWEEN MR. SMITH AND PROMOTERS OF NLP FILTERS AND CONDITIONERS

In Dec 2016, a Flint family began posting videos on Facebook, praising a whole-house filter "package deal" from a company called NLP Aqua Solutions that would cost US$11,300-US$13,800 per Flint household to install (Murphy 2016; Edwards and Roy 2017b). Mr. Smith and the NLP company representatives appear in some of the videos (Murphy 2016; Murphy 2017), including one where the resident read aloud from a letter purportedly from Mr. Smith stating that:

> "[NLP] is the first filtering technology I have reviewed with test results that makes me comfortable in saying the water is safe for drinking, showering, and bathing. […] I look forward to taking a shower at your house and drinking the water after the treated NLP Aqua Solutions technology. (Withstand With Wolves 2017)"

Given Mr. Smith's affiliation with Ruffalo's Water Defense, this statement seemed just one step removed from a celebrity endorsement of a for profit, proprietary product amidst a federal emergency, and widespread fear of bathing/showering that Water Defense itself had exacerbated. The Flint residents also referenced Smith as stating their specially filtered water is "safer than bottled water (Withstand With Wolves 2017)." We then determined that these filters promoted by Smith, cost 5-7X more than other off-the-shelf filters that removed even more contaminants. The package deal also included water treatment devices called "conditioners," that the company sales literature says could soften water without using any chemicals and protect plumbing and appliances from damage. The NLP company website made claims that their specially conditioned water boosted plant root growth, and even increased milk production if their water was consumed by cows. We then tested this device in the laboratory and found it did not perform as claimed in scientific numerous dimensions of performance—consistent with other internet sources claiming the NLP conditioner was "junk science (Lower 2013; NLP Aqua Solutions 2016; Murphy 2017; Edwards and Roy 2017b)."

Countering and exposing what we considered were obvious profit-minded, unscientific, and harmful activities by Mr. Smith of Water Defense, also resulted in receipt of numerous "Cease and Desist" letters from Mr. Ruffalo's lawyers. We then uncovered additional hard evidence of financial conflicts including social media postings of a filter package deal where US$2,100 of the cost was earmarked for Smith and his sponge testing, and letterheads of lab reports handed to Flint residents by Smith that had his for-profit "Aquaflex" address on them (Edwards and Roy 2017b). These revelations, finally resulted in Ruffalo's non-profit and Mr. Smith parting company in June 2017,

presumably since this violated their commitment of not "hav<ing> any […] connection with [Aquaflex] (CNN, Personal Communication, June 7 2017; Water Defense, n.d.)".

CITIZEN SCIENCE MISCONDUCT?

"Tell a lie once and all your truths become questionable." – Anonymous

In our initial sampling efforts, all parties were completely focused on exercising extreme care to collect samples correctly, and residents contributed to that process by development of tamper resistant sample kits, screening videos on proper sampling techniques to residents whenever possible, or conducting the sampling themselves when some residents might not have followed the protocols. They correctly anticipated, that if our team found a citywide lead problem, both our motivation and methods would be questioned and they wanted data to withstand scrutiny. Afterall, our team was directly challenging the power and conclusions of the state MDEQ and EPA. When one reporter asked "How do you know Flint residents are not just adding lead to the water to gain attention?," we not only cited the care the residents showed, but also some high water lead samples collected completely by our Virginia Tech team.

After the initial triumph of our citywide sampling event and unprecedented publicity, the tables were completely reversed—nearly any sampling result put forth by residents, or hypothesized link between ailments and the water, could be broadcast in the national and international media. Water Defense and some citizens, actively began to promote improper sampling methods that obtained artificially "high" results which could be used to gain attention or push an overtly biased agenda. It is noteworthy that all of these case studies fully realize the Riley et al (2016) model of "citizen engineering," with a primary goal of "undermining expertise" and "disrupting communities."

Case 1

Resident A confirmed to us in writing in 2015 that her home had a copper service line and modern lead-free plumbing (i.e., no lead solder) inside her house. The maximum water lead level detected at her kitchen faucet from five samples collected during the crisis period with highly corrosive water was 8 ppb. This was well below the 15 ppb action level and consistent with her initial claim of no major water lead sources in her plumbing. Her results changed dramatically after she began to openly collaborate with Mr. Smith, and it was later determined that she started collecting samples from a hose bib in her basement which is an improper sampling location according to EPA that creates false positive (high lead) results (Edwards 2017). Despite willfully violating the written protocols in test kits provided by the State of Michigan or Virginia Tech, the results were broadcast by Mr. Smith, Mr. Ruffalo on social media with no mention of the modified sampling approach. As time went on this residents' lead results went up to 150 to 1740 ppb lead (Figure 7-2), and she held "press conferences" advertising the improper results and disseminating them via gullible national media with an assertion that Flint water quality was getting worse with time (Mays 2016b; Smith 2016a; Ruffalo 2016; PRWeb 2016; Edwards 2017).

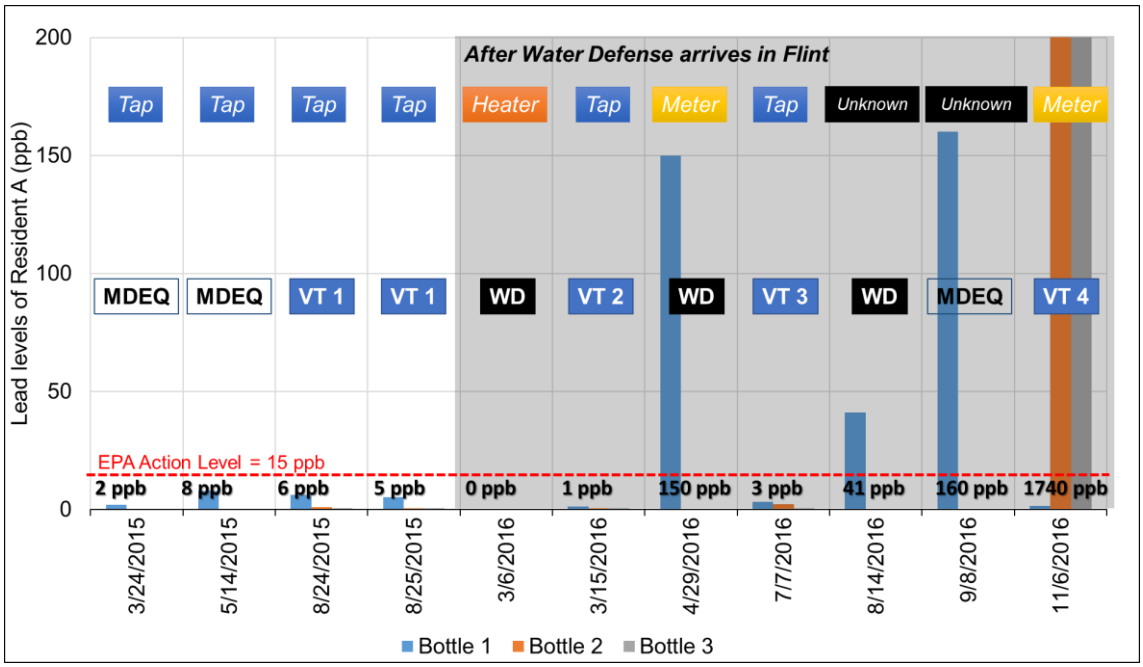


Figure 7-2. Resident A's lead levels during the Flint Water Crisis. For every test, the top box indicates the sample collection location and the bottom box shows testing agency, including MDEQ, Virginia Tech, and Water Defense. The highest lead value obtained per sampling event is stated above the horizontal axis.

This resident also attempted to use these high lead results in a manner that illustrated a possible financial conflict of interest. For example, in one social media posting, she cited her result, and a desire to be given a free service line replacement which at the time was prioritized for residents who had dangerous lead pipe (Walters 2017). When other residents called out this opportunism, Resident A deleted that posting. She was also lead plaintiff on several lawsuits (Mays, et al. v. City of Flint, et al., Genesee County Circuit Court; Mays, et al. v. Snyder, et al., Michigan Court of Claims; and Mays, et al. v. Snyder, et al., U.S. Federal Court for the Eastern District of Michigan) in which high lead data played a role (Flint Water Class Action 2016-17). At the launch event of the LIFETIME movie "FLINT," she cited high water lead monitoring data to assert in the media that "[Flint residents] are still being poisoned" as late as Oct 2017 (Mcfarland 2017). Other "citizen engineering" comments from this resident, included claims that the Flint water meeting federal standards was transforming bathroom showers into "gas chambers" and, therefore, "until every single piece of plumbing is replaced, [Flint residents] are in danger (Lifetime 2017; TATM 2017)." She openly attacked all the agencies, Virginia Tech and other residents who presented data indicating the water quality was improving. Moreover, this resident's actions were openly embraced and encouraged by Riley's colleagues (Lambrinidou 2016-17; Mays 2016-17).

Case 2

Resident B stated on social media September 16 2017, that he gamed the Virginia Tech protocol in Round 5 (Aug 2017), by collecting water samples from a different building in Flint (Sylvester Broome Center) instead of his own house as represented to our team and required by the protocol (Hodges 2017). Because the water lead levels from both Round 4 testing at his house (Nov 2016) and Round 5 testing at the other Flint building, came back below detection limit (<1 ppb), the resident opined online that the VT sample results were not trustworthy because "it's odd to me that both water samples <from different locations> are exactly the same." That was not true, but all data were consistently below the detection limit (Figure 7-3).

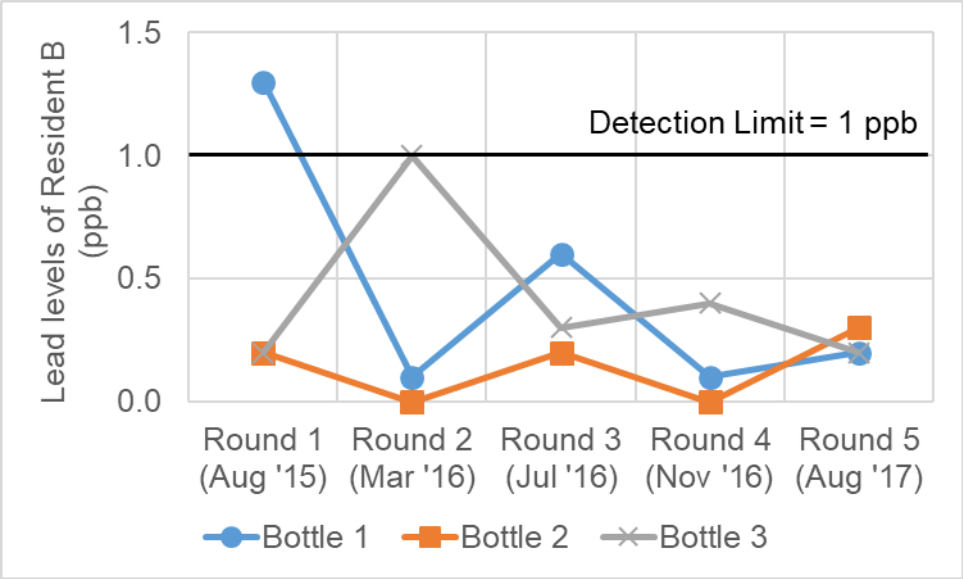


Figure 7-3. Lead levels for water samples obtained from Resident B through all five rounds of citizen testing. ICP-MS data for Resident B's house (in Round 4) and from the other building (in Round 5) are clearly different.

Case 3

Resident C's home, also serviced by a copper service line, had a water lead level trend even more startling than Resident A. During the recovery phase of the system prior to compliance with the LCR in July 2016, when there was still a citywide problem, 12 analyzed water samples from this home were between 5-44 ppb. However, 10 months after Resident A first publicized Mr. Smith's approach to collecting improper samples that obtained higher lead data, C's lead levels reached and surpassed hazardous waste levels (>5,000 ppb) in July 2017, causing both alarm (Figure 7-4) and widespread media coverage (Pierret 2017).

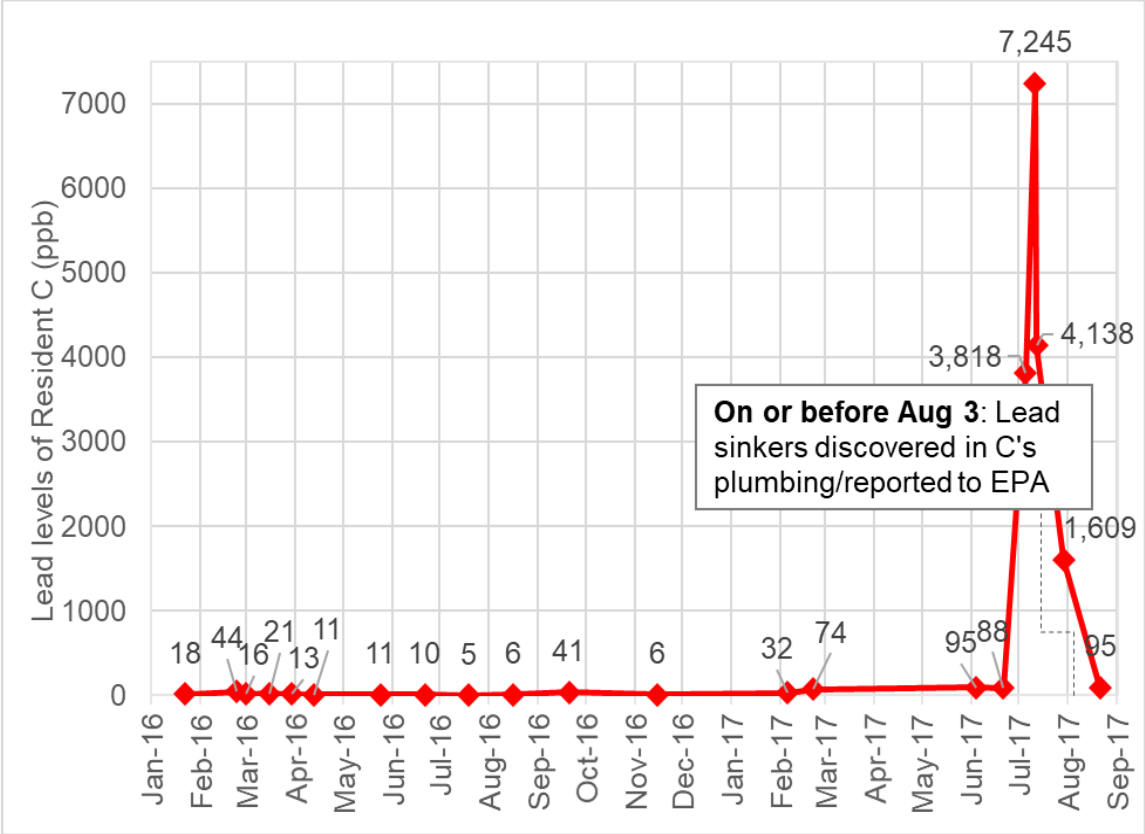


Figure 7-4. Resident C's lead levels during and after the Flint Water Crisis 2016-17 (Source: MDEQ, social media postings)

Perplexed as to how this could be, we submitted a Freedom of Information Act (FOIA) request to the US EPA that revealed Mr. Smith knew about two lead sinkers found inside her plumbing in early August 2017 (Edwards and Roy 2017c). Before we made the FOIA public, Resident A, Mr. Chariton and other residents had broadcast Resident C's high lead results on social media, and the data was also cited in the LIFETIME movie to support the assertion that the water lead crisis was continuing in Flint (Cher et al. 2017; Hammond 2017; Roy and Edwards 2017d). We also revealed that Resident C also had overt financial conflicts of interest, as evidence by launch of a GoFundMe online fundraiser that cited her high lead results, and in interviews where she claimed that all "[water] mains, service lines, everybody's […] hot water heaters, refrigerators, washers, everything" should be replaced (ECH 2017). C is also part of the class action lawsuit along with Resident A (Edwards and Roy 2017d).

The timeline of social media postings, also documented formation of a Riley "citizen engineering" hypothesis, whereby Flint residents were getting lead poisoned simply by taking a shower (Smith 2016b; Marx 2017; Roy and Edwards 2017d). This hypothesis had been frequently cited publicly by Mr. Smith, and the fact it was contradicted by decades of sound research from all reputable agencies, scientists and engineers never phased him in the slightest. Attempting to take Riley's theory that "non-engineers can make crucial contributions that improve engineering practice" to an extreme, Resident C

apparently took on the role of research pioneer – just six weeks after announcing her hypothesis on social media, she obtained documentation of her blood lead poisoning result that was immediately announced on social media: "you most certainly can get lead poisoning by showering in toxic water! (Marx 2017)" Importantly, during this time, no mention was made of a discovery of lead sinkers inside her plumbing by anyone (Resident A, Resident C, Mr. Smith or Mr. Chariton).

After we published the FOIA with videos of lead sinkers found in her plumbing and laid out the timeline of events online, including the timing of her GoFundMe launch, Chariton wrote that the sinkers had "NOTHING to do with [Resident C's] high lead-levels" but her lawyer barred her from talking to the media (Conat 2017; Fonger 2017b; Roy and Edwards 2017d). The lawyer first claimed that no lead sinkers were found inside C's bathroom tap, but then retracted the statement, and, finally, made a claim that the lead sinkers would not matter anyway because they would not leach any lead. We disproved that statement with our own experiments using lead sinkers and one of us (MAE) took a shower in toxic levels of lead with no detectable biological impacts. Her lawyer then labeled the lead sinker story a "distraction" from the class action lawsuit Resident C was party to,and suggested that "a big defamation lawsuit" could be filed against us for exposing the presence of lead sinkers and posting the timeline. The resident's GoFundMe page disappeared within approximately two weeks of our posting (Roy and Edwards 2017d). The state has declined to release other emails associated with this case under the Freedom of Information Act, stating this "could jeopardize an investigation by [EPA's] Criminal Investigation Division (Fonger 2017c)."

SOBERING LESSONS ON CITIZEN ENGINEERING AND SCIENCE ANARCHY FROM POST-EMERGENCY FLINT

"There is nothing to fear except the persistent refusal to find out the truth." ― Dorothy Thompson (BrainyQuote 2018)

The abuse of "citizen science" by a non-profit, an online news network, a few residents and anarchist academics practicing "citizen engineering," highlight legitimate concerns and ethical dilemmas surrounding citizen science. This section attempts to describe features of good citizen science, reveals current postmodern efforts towards undermining scientific expertise that can cause citizen science to be unscientific and generate harm, and provides a conceptual framework for scientists considering collaborations with activists, especially in cases involving environmental justice.

Characteristics of Quality Citizen Science Projects

Freitag and colleagues (2016) list 12 strategies to enhance credibility of citizen science projects, including **prior expertise** of project leaders, substantial training of citizen scientists, science advising to strengthen data collection, peer-oversight between citizen scientists, quality assurance protocols, and cross-comparison of citizen science data with data from professionals. This approach emphasizes rigor and objectivity, and views science as a truth-seeking exercise, albeit subject to the same limitations and biases that

face all scientists. We evaluated the initial citizen science collaboration that exposed the Flint Water Crisis against Freitag et al.'s criteria and believe it satisfied all 11 applicable criteria. The Water Defense-TYT Politics, Citizen A and Citizen C "citizen engineering" actions, in contrast, satisfied none (see Table 7-1). Above and beyond the excellent framework of Freitag, the Flint experience has highlighted other (qualitative and ethical) characteristics of good citizen science that are lacking when "citizen science" can be high-jacked by science anarchists and advocates with agendas other than truth-seeking. These include scientific rigor, willing reporting of evidence counter to one's goals (i.e., intellectual honesty), working in only one's competence area, transparency, obligation to correct misinformation and addressing conflicts of interest.

Table 7-1. Strategies from Freitag and colleagues (2016) used to assess the initial Virginia Tech-Flint residents "citizen science" collaboration and Water Defense-TYT Politics "citizen engineering" practices

No.	Strategies for demonstrating credibility	Assessment of VT-Flint citizen science collaboration	Assessment of Water Defense-TYT citizen engineering
EARLY ACTIONS			
1	Prior expertise (is there a "formalized minimum standard that volunteers must meet to participate?": Yes, No)	Not Applicable; water samples for lead are normally collected by residents under the LCR	No; e.g.: Waterbug and encouraging of improper sampling
2	Training ("time investment" to train volunteers: None, Low, Medium, High)	Low; required viewing of YouTube sampling video	None for Waterbug.
3	Science advising ("partnership with a university lab", etc.: Yes, No)	Yes: with Virginia Tech scientists	No; No water scientists on team
IN THE FIELD			
4	Ranking system (Volunteers designated as "experts" after gathering experience or passing tests: Yes, No)	Yes: for select residents. Flint residents paid by EPA to execute citizen sampling.	No; Any citizens can be experts and "take water quality testing into their own hands" using WaterBug®
5	In-person oversight ("expert" volunteers to "directly oversee data collection" to minimize data collection errors: Yes, No)	Yes; cross-checking survey data between citizens	No; Mr. Smith did not have expertise in EPA protocols.
6	Retraining (Advancement of volunteer skills through more trainings, readings, etc.: Yes, Optional, No)	Yes; select residents sampling for chlorine.	No; WaterBug® was hypothesized useful for heavy metals, pathogens, DBPs
7	Technological aids	Yes; Mostly using	No; "independent lab"

	(Simplifying data collection using technology: Yes, No)	Excel	provided data dump in "lab reports" of up to 97 pages
IN THE OFFICE			
8	Validation of observations: (Checks for human error and "statistics-driven flagging of incorrect data", etc.: Yes, No)	Yes; Attempt for rigorous evaluation of collection methods for each sampled home	No
9	Cross-comparison (Comparing volunteer data to that collected by scientific experts to demonstrate credibility of "methods and data": Yes, No)	Yes; samples collected from same locations by citizen scientists and experts. 3rd parties.	No
10	Publication (external peer-review and/or publishing of data and findings: Yes, No)	Yes; several papers published in respected journals	No; no journal articles/peer-review of water quality data
11	Management use (Decision-makers use citizen science data: Yes, No)	Yes; informed Federal Emergency declaration and EPA funded work	No; Attempt was made to undermine decision makers.
12	Quality assurance protocol (Standard QA practice to "calibrate methods, technology and practice over time": Yes, No)	Yes; as per Standard Methods and EPA guidelines	No; WaterBug® not vetted against established EPA/ WHO guidelines

Post Modern Undermining of Expertise and The Dunning-Kruger Effect

Undermining expertise and the power associated with it, is raison d'etre of science anarchists (Riley et al., 2015, 2016, 2017). It could be argued that citizen science attempts to reduce this very worrisome power and expertise gap through collaboration, respect for an individual's experiences and observations, and working together to create new knowledge. In contrast, postmodern science anarchists, overtly act to "undermine engineering expertise" attempting to make all views equal, by insinuating that "engineering has already taken […] the side of the mainstream, of those in power" and, therefore, it is necessary to attack the very concept of expertise itself (Riley and Lambrinidou 2015; Riley et al. 2016). The strident nature of Riley and colleagues perspective on this issue, is captured by a live-tweet from a self-described "Christian anarchist" at a recent Riley keynote address: "@riled1 My professional expertise as a thermodynamic engineer is no more important than the expertise of activists. YES YES YES (Arnold 2017)."

Our examples illustrate a populist, postmodernist, anti-elitist social science movement that challenges conventional expertise, scientific rigor and organized knowledge. Along the citizen science and citizen engineering spectrum the term "democratization" of

science truly means different things to different people. To most it means bringing scientific methods and principles, to study of problems that can only be solved by collaborations between citizens and scientists, sometimes in communities underserved by traditional science (Cooper 2017). To others it represents an ideal of science anarchy with an explicit goal of "disrupting expertise in the classroom and communities" or "decolonizing" science (Lambrinidou 2016; Lambrinidou 2016-17; Riley et al. 2016). And anything done with that goal is right and justified, as illustrated by Ruffalo's statement that "there is nothing wrong with giving people data" even if it likely contributed to public health harm (Water Defense 2016a).

Interestingly, after taking Riley's semester long course entitled "Citizen Engineering: Disrupting Expertise in Classroom and Community," the researchers conclude that: "***This population of students struggled with…the central argument of the course that engineering ought to be democratized…"*** and listed strategies that might better achieve that objective (Riley et al. 2016). But the question as to whether this is a worthy goal in the first place is never addressed by Riley and others. Should there be efforts directed to "undermining expertise of brain surgeons" or "undermining expertise of airline pilots," in the midst of brain surgery or while a plane is in flight? If experiences in Flint post-emergency are any guide, Riley's students were correct that "citizen engineering" is a dangerous concept they should struggle with.

Even the best scientists, after decades of training, are still humans and, therefore, must always be on guard to minimize the likelihood of self-deception (Nuzzo 2015; Mirowski 2017). A good scientist has developed self-awareness, a strong sense of humility, especially in their proven area of expertise (Margolis 1997; Kruger and Dunning 1999). Scientists are looked at as "purveyors of truth" (Marmot 2017), which is indeed an ideal worth aspiring to while communicating both facts and uncertainties. This was also evident in an early 2016 Flint poll that showed "University Scientists" (including Virginia Tech) as being "Helpful and Trusted" by Flint Residents (Gray et al. 2016)." The general public does trust this expertise, with Pew and Gallup polls in 2016 showing that over 75% Americans trust scientists to act in the larger interest and 65% Americans rate engineers' honesty and integrity at 'High' or 'Very High' (up from 48% in 1976) respectively (Gallup 2016; Kennedy 2016). In 45 years, "science is the one [public] institution that has not suffered any erosion of public confidence (Dastagir 2017)." Similar trends can be seen in Europe (European Commission 2012).

These examples collectively illustrate the *Dunning-Kruger Effect* (Figure 7-5) that is summarized: "Those with limited knowledge in a domain suffer a dual burden: Not only do they reach mistaken conclusions and make regrettable errors, but their incompetence robs them of the ability to realize it" (Kruger and Dunning, 1999). With no scientific background or legitimate experience in water quality or engineering, Mr. Smith (Water Defense), Mr. Chariton (TYT Politics), Resident A and C were truly "unskilled and unaware of [their incompetence]." When they took the spotlight and engaged in "citizen engineering" in post-federal emergency Flint, the results did sometimes achieve the goal of "disrupting expertise" and "communities," but without making any "crucial contributions that improve engineering practice (Riley et al. 2016)." Science anarchists

are not only more prone to unconscious biases and logical fallacies, but in many cases they are driven and defined by them.

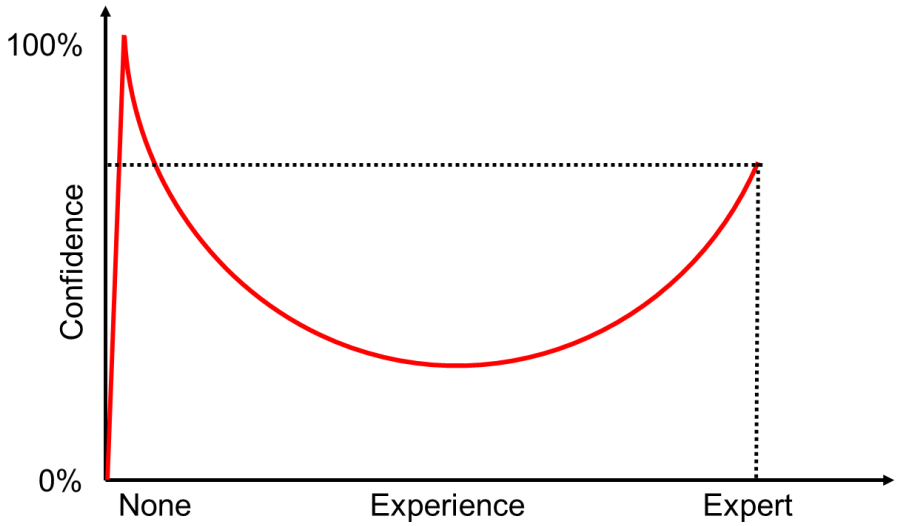


Figure 7-5. The Dunning-Kruger Effect (illustrative simplified version)

Citizen Science with/vs Citizen Engineering: Collaborations and confrontation that are sometimes necessary but fraught with peril.

"Democracy cannot function when every citizen is an expert. Yes, it is unbridled ego for experts to believe they can run a democracy while ignoring its voters; it is also, however, ignorant narcissism for laypeople to believe that they can maintain a large and advanced nation without listening to the voices of those more educated and experienced than themselves." – Tom Nichols (Nichols 2017)

We have been outspoken about the danger of perverse incentives in modern academia, where promotion and tenure are increasingly tied to quantitative metrics including research papers and funding dollars, and which in turn likely increase the likelihood of misconduct and threaten scientific integrity (Edwards and Roy, 2017e). Flint demonstrates that similar perverse incentives also exist for citizen scientists, if they are incentivized to find answers that lead to financial rewards and media attention (i.e., a LIFETIME movie deal, class action lawsuit).

However, we did collaborate closely and successfully, for years with "citizen engineering" proponents in exposing the Washington D.C. lead in drinking water coverup (Lambrinidou and Edwards 2013). And Resident A was a valued member of our initial Flint Citizen Science team until parting company after the declaration of the Federal Emergency, at which point we worked alongside the agencies that we had previously attacked, whereas resident A and some others stayed on the attack even after the heroic EPA whistleblower was recruited to become the face of the agency response (Fonger 2016). Which raises the question "When are collaborations between citizen engineers and citizen scientists productive, and when will they "go wrong" and end in confrontation?

Our interpretation is based on years of experiences with a range of residents and self-identified activist academics. A key is to understand that scientists and citizen scientists highly value the aspirations of objectivity, rigor, truth-seeking and acquiring expertise (Figure 7-6), whereas activist academics, pseudoscientists or citizen engineers value subjectivity, "other ways of knowing", their personal version of social justice, and undermining expertise/power (Riley and Lambrinidou 2015; Riley et al. 2016; Riley 2017a).

These usually divergent values are highly complementary in a narrow set of circumstances, including collaborations to expose government science agency misconduct or an environmental crisis—illustrative examples include our work exposing the Washington D.C. lead in water cover-up or the 2014-2015 Flint Water Crisis (Quadrant 4). If pseudo-scientists or activist academics collaborate with citizen engineers, they can sometimes effectively disrupt communities and expertise, as in the case of "bathing and showering fears in Flint," to the detriment of public health (Quadrant 1). Quadrants 2 and 3 indicate a mismatch where confrontation is likely and necessary. Such as the case in which the indicted State of MI scientists were using citizen scientists to gather data to claim the water was safe when it was not under the EPA LCR (Quadrant 2).

Quadrant 3 represents an existential conflict of canons and values between citizen science and citizen engineers. The first canon of civil engineering, to protect the public welfare, ethically obligated us to confront and then directly undermine activists and pseudoscientists who were directly endangering public health of the community (i.e. possible contributing to shigella and other outbreaks). But Riley and Lambrinidou, borrowing from the social workers code of ethics, propose "social justice" as a new core value for engineers, to counter "the profession's tendency to marginalize, ignore, silence,…Local knowledges and scientific counter-knowledges that depart from dominant paradigms of engineering thought and practice and, at times, even challenge or oppose the profession's status quo (Riley and Lambrinidou 2015)." To Riley and Lambrinidou, our upholding the actual First Canon of civil engineering ("To hold paramount the safety, health and welfare of the public"), violated their over-riding "social justice" Canon that all expertise should be equal. Indeed, even after Mr. Smith and Mr. Chariton had been completely and publicly discredited, and the citizen engineering of Resident A and C had been exposed, Riley live tweeted that our undermining of these individuals represented "structural bullying" analogous to the abuses of those engaging in sexual harassment and assault: "#metoo" (Riley 2017b; Edwards et al. 2018). At no point did Riley or Lambrinidou, express anything but solidarity, with Flint's activist citizen engineers (Lambrinidou 2016-17).

Figure 7-6. The Scientific Goal v/s The Activist Goal – A conceptual framework of when interests align and when they do not, with real world examples from the Flint Water Crisis. Quadrant 4 is only circumstance where science anarchists and scientists goals are in alignment

THE FUTURE

"A code of ethics cannot be developed overnight by edict or official pronouncement. It is developed by years of practice and performance of duty according to high ethical standards. It must be self-policing. Without such a code, […] a group soon loses identity and effectiveness." - Silas L. Copeland (AUSA 2009)

The Flint case study reveals both the promise and perils of citizen science, as a tool for social justice, scientific advancement and a general public good. Some argue citizen science is not about producing real knowledge, but "rejigging power relations" to get (often, unpaid) citizens to produce data that benefits private corporations and academic researchers, with the "citizen herself […] almost entirely absent", and the democratization of science argument is mere window dressing (Mirowski 2017). But the citizen science collaboration that uncovered environmental injustice in Flint was noteworthy, because the team focused on knowledge sharing and collecting data upon which lives literally depended, guided in an evidence-based battle with help from Virginia Tech scientists who had years of preparation for such a high stakes battle.

But, overall, it does seem that "citizen science has not addressed the incongruity of mimicking scientific practice while side-stepping the need to know anything about science (Mirowski 2017)."

The work also showed that no one is above the temptation to cheat, whether citizen or scientist, and those who consider citizens as incorruptible paragons of wisdom and virtue, are at least as misguided as those who tend to believe the same of scientists and engineers. It is important to note that Water Defense, TYT Politics and Flint Residents A-C, had no scientific reputation to lose. As a result, citizen science, in and of itself, may be

even less capable of self-policing than normal science. Not surprisingly, a form of social anarchy, followed the practice of science anarchy in post-emergency Flint, and the results were tragic.

ACKNOWLEDGEMENTS

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CHAPTER 7. AN EVALUATION OF THE READABILITY OF DRINKING WATER QUALITY REPORTS: A NATIONAL ASSESSMENT

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ABSTRACT

The United States Environmental Protection Agency mandates that community water systems (or water utilities) provide annual consumer confidence reports (CCRs) – water quality reports – to their consumers. These reports encapsulate information regarding sources of water, detected contaminants, regulatory compliance, and educational material. These reports have excellent potential for providing the public with accurate information on the safety of tap water, but there is a lack of research on the degree to which the information can be understood by a large proportion of the population. This study evaluated the readability of a nationally representative sample of 30 CCRs, released between 2011 and 2013. Readability (or 'comprehension difficulty') was evaluated using Flesch–Kincaid readability tests. The analysis revealed that CCRs were written at the 11th–14th grade level, which is well above the recommended 6th–7th grade level for public health communications. The CCR readability ease was found to be equivalent to that of the *Harvard Law Review* journal. These findings expose a wide chasm that exists between current water quality reports and their effectiveness toward being understandable to US residents. Suggestions for reorienting language and scientific information in CCRs to be easily comprehensible to the public are offered.

KEYWORDS: consumer confidence reports, health communication, readability, tap water, water quality

INTRODUCTION

The consumer confidence report (CCR) rule of 1998 (Federal Register 1998) requires all community water systems (i.e., water utilities) to provide annual water quality reports to their consumers. These reports contain information regarding water source, level of any detected contaminants, compliance with drinking water regulations, and relevant educational information. All water utilities and retailers that provide at least 15 service connections or regularly serve at least 25 residents year-round fall under the purview of this rule (US Environmental Protection Agency 1999). Their overarching purpose is to 'improve public health protection by providing educational material to allow consumers to make educated decisions regarding any potential health risks pertaining to the quality, treatment, and management of their drinking water supply' (US Environmental Protection Agency 2002).

The need for providing water quality information to consumers has been repeatedly emphasized (Odugbesan et al. 1998; Roper Starch Worldwide 1999; Benson et al. 2002; Means et al. 2002; Meyer-Emerick 2004; Blette 2008); this communication should also be transparent (Pene & Levi 2011). Consumers want more information about their tap water (Roper Starch Worldwide 1999), and have expressed concerns about its quality (Means et al. 2002). The CCR acts as an agent toward improving the public's confidence in their tap water and prompting increased water consumption.

Tap water in the USA is readily available, regulated and monitored for safety, calorie-free, and low cost. Yet, on a given day, half of the US population over the age of 2 years consumes sugar-sweetened beverages (SSB), which represents a significant source of daily calories (Ogden et al. 2011; Huth et al. 2013). 'Drink water instead of sugary drinks' is one of the seven key selected messages for consumers in the Dietary Guidelines for Americans (US Department of Agriculture & US Department of Health and Human Services 2010). Unfortunately, SSB manufacturers are not required to publish a beverage quality report while perceptions of water safety based on difficult to read CCRs could represent a barrier to promoting water as an alternative to SSB. The perception that local tap water is unsafe varies by region, and is more common among young adults, those with lower income levels, and among racial/ethnic minorities (Onufrak et al. 2014). Americans have been consuming less tap water while consuming more bottled water and other beverages due to perceived health and safety concerns (Azoulay et al. 2001; Hu et al. 2011). Moreover, the bottled water industry has had a negative influence on perceptions about drinking water quality that has been difficult for water utilities to counteract (Meyer-Emerick 2004).

Efforts to build trust in public water utilities to overcome tap water 'avoidance' and reliance on bottled water are needed (Scherzer et al. 2010). The public has to be an 'informed partner' if the utility wishes to incorporate new treatment techniques to meet new regulations, undertake expansions of the plant capacity, effectively handle water contamination events, and raise water rates to meet all of the above (Glicker 1992). 'Persevering trust (or distrust), evocation of negative beliefs about risk from any

discussions of ‘contaminants’, or personal experience’ are some factors that may dominate CCR reception by the public (Johnson 2003).

One solution would be for health officials and community leaders to assure the public that tap water supplies are safe (Hu et al. 2011). Implications associated with poor communication can be serious: economic impacts on low-income homeowners, for instance, who may seek more costly sources of drinking water in search of true or perceived safety if they do not have confidence in the safety of their tap water (Blette 2008). For a random sample of New Jersey residents, Johnson (2003) found that reading water quality reports did not shift customers' evaluations of water quality and utility performance from the evaluations of those in the control group, who did not see a report. Water utilities should, thus, actively ensure their consumers receive and understand their CCRs in order to positively impact public perception.

Presenting information that is understandable and meaningful to scientists, engineers, administrators, and to the general public is a challenge for the water quality personnel (Mackenthun 1969). Some important considerations that should be addressed while developing CCRs include:

a) readability levels and health literacy of the public;

b) language complexity and use of technical jargon/risk information;

c) informational design and graphics;

d) clarity in addressing behavioral recommendations and multiple main messages;

e) public distrust of tap water based on media reports, prior contamination events, and public perceptions.

The United States Environmental Protection Agency (US EPA) encourages usage of its CCR iWriter software, available on the internet, for maintaining a standardized format for information delivery (US Environmental Protection Agency 2013). While this guarantees that consumers are receiving comparable information, it also limits the ability to educate diverse groups (Meyer-Emerick 2004) and does not include standards to improve the comprehension of CCR messaging. To our knowledge, the effectiveness of published CCRs and the mandated EPA language has not been evaluated. Thus, our objective was to assess the readability of CCRs to determine the degree to which the content is accessible to a broad cross-section of the population, and to compare results to those recommended for public health communications.

MATERIALS AND METHODS

Selection of CCRs.

Three water utilities were selected for each of the 10 US EPA regions – one from each size category (Figure 8-1). Size categories for the utilities are based on the population size they serve: medium (3,301–10,000); large (10,001–100,000); and very large (100,000+). Their population size (and, thus, size category) were confirmed through the US Environmental Protection Agency's (2014b) and water utilities' websites and/or telephonic/email exchange with utility personnel. Consequently, a total of 30 water utilities materials were evaluated. The CCRs were selected from years 2011 to 2013 and obtained through the US Environmental Protection Agency's (2014b) and water utilities' websites. The content of these reports ranged from two-page text blocks in Microsoft Word to illustrated 10+ page reports elaborating information such as source water to plant expansion plans.

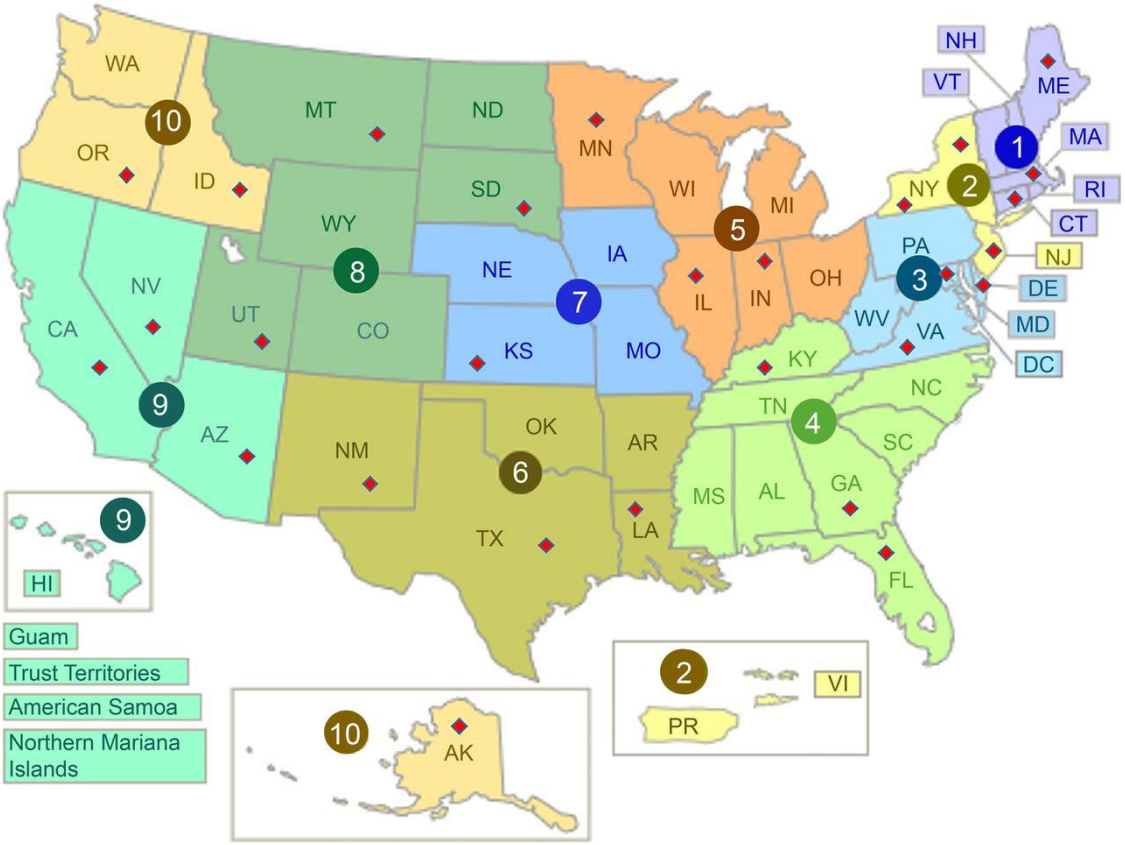

Figure 8-1. Map of US EPA regions and the states in which the selected CCRs are located – signified by the diamonds (adapted from US Environmental Protection Agency (2014a)).

Assessing readability.

Jordan (1998) specifically emphasized the importance of readability of CCRs. The Flesch–Kincaid readability (FKR) tests were used to evaluate readability of the CCRs. These tests are widely used in education, publishing, business, healthcare, the military, and industry for all forms of written communication (Kincaid et al. 1975) including print and online media. When Flesch originally released these formulae, Swanson & Fox (1953) estimated that using them could increase reading comprehension by up to 60%. The FKR tests comprise:

(a) Flesch reading ease (Equation (1), scaled 0–100; a higher score equates to better comprehension; and

$$Flesch\ Reading\ Ease = 206.835 - 1.015\frac{(Total\ words)}{(Total\ sentences)} - 84.6\frac{(Total\ syllables)}{(Total\ words)} \quad (1)$$

(b) Flesch–Kincaid grade level (Equation (2) which gives a 'grade level' equivalent to the USA school grade system.

$$Flesch - Kincaid\ Grade\ Level = 0.39\frac{(Total\ words)}{(Total\ sentences)} + 11.8\frac{(Total\ syllables)}{(Total\ words)} - 15.59 \quad (2)$$

The relationship between the reading ease, grade level, and examples of publication type is presented in Table 8-1. The FKR tests are reliable, widely used, and correlate well with comprehension measured using reading tests (Chall 1958; Klare 1963; DuBay 2007). With regard to recommendations, the National Institutes of Health (2013) advises that health communication materials be written at a ~6–7th grade level, and health literacy experts recommend that materials be targeted to the 5th–6th grade reading level (Conrath et al. 1996; Weiss & Coyne 1997). The average American reads at the 7th–8th grade level (National Center for Education Statistics & Kutner 2006). The State of the Union addresses of recent US presidents including Bill Clinton, George W. Bush, and Barack Obama corroborate with these levels since they were written at 8th–10th grade levels as well (The Guardian 2013).

Table 8-1. Analysis of readability of adult reading materials (modified from Flesch (1949))

Style	Flesch reading ease	Average words/ sentence	Magazine type	Example	Estimated school grade completed
Very easy	90–100	8 or less	Comics		4th
Easy	80–90	11	Pulp fiction	*Harry Potter and the Sorcerer's Stone*, chapter 2	5th
Fairly easy	70–80	14	Slick fiction		6th
Standard	60–70	17	Digests	*Reader's Digest*	7th–8th
Fairly difficult	50–60	21	Quality	US Department of Defense documents/manuals; life insurance policies in the State of Florida (ease >45)	Some high school
Difficult	30–50	25	Academic	*Harvard Law Review* articles	High school/some college
Very difficult	0–30	29 or more	Scientific		College

Additional data from Ressler (1993), US Department of Defense (1995), DuBay (2007), Kunz & Osbourne (2010), State of Florida (2013), and the website ReadabilityFormulas.com.

The CCRs for chosen utilities were available either as portable document format (PDF) or Microsoft Word (DOC) files. The PDF versions were converted to DOC file using select online tools: PDFOnline.com, FreePDFConvert.com, and PDFBurger.com. Documents were inspected to ensure continuity of all paragraphs and text blocks were intact before running the FKR tests using the readability statistics function in Microsoft Word 2013.

RESULTS AND DISCUSSION

The CCR reading ease ranged from 26.3 to 43.8 (median = 36.45), which is within the academic/scientific level (Figure 8-2). To provide context, the *Harvard Law Review* journal has a reading ease in the low 30s (Kunz & Osbourne 2010). Similarly, the CCR grade level ranged from 11.1 to 14.3 with a median value of 12.65 (Figure 8-3); this is substantially higher than the NIH's recommended 6th–7th grade level for health materials (National Institutes of Health 2013).

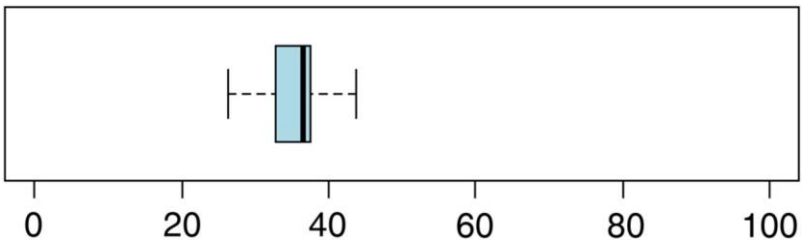

Figure 8-2. Box plot showing the reading ease range of 30 CCRs.

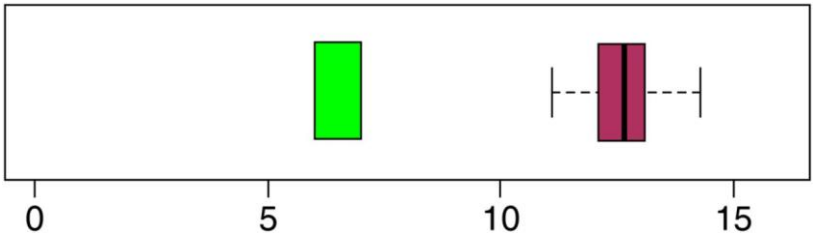

Figure 8-3. Box plot showing the grade level range of 30 CCRs (the box on the left signifies NIH's 6th–7th grade level recommendation for health materials).

An analysis of the reading ease and grade level medians at the utility size level revealed no differences from those of the overall sample size values. The reading ease and grade level of all three utility sizes (medium, large and very large) ranged from 35.5 to 36.8 and from 12.4 to 12.85, respectively. While CCRs from the large and very large categories were generally more detailed, illustrated and visually pleasing, their FKR results were comparable to that of medium-sized utilities.

Such high scores could partly be attributed to mandated US EPA language seen in several CCRs. Below is an example of a typical CCR paragraph under the category ‘general information about your drinking water’:

> "All drinking water, including bottled water, may reasonably be expected to contain at least small amounts of some contaminants. The presence of contaminants does not necessarily indicate that the water poses a health risk. Some people may be more vulnerable to contaminants in drinking water than the general population. Immuno-compromised persons such as persons with cancer undergoing chemotherapy, persons who have undergone organ transplants, people with HIV/AIDS or other immune system disorders, some elderly, and infants can be particularly at risk of infections. These people should seek advice about drinking water from their health care providers. For more information about contaminants and potential health effects, or to receive a copy of the U.S. Environmental Protection Agency (EPA) and the US Centers for Disease Control (CDC) guidelines on appropriate means to lessen the risk of infection by *Cryptosporidium* and microbiological contaminants call the EPA safe drinking water hotline at 1-800-426-4791."

With an average of 24.8 words per sentence, this paragraph has a low reading ease of 12.9 and a high grade level of 17.6. Unfortunately, when text exceeds one's reading level,

consumers usually stop reading (DuBay 2007). A study (Johnson 2003) on a random sample of New Jersey residents getting CCRs found that many respondents had trouble identifying presence/absence of substance amounts or violations, despite their seeming obviousness (e.g., in a 'bottom line' summary on the front page of each report). This seemed to suggest they were not processing the information carefully, although their response patterns were not substantially different from the group responding as a whole. Jordan (1998) advised usage of familiar units, explaining action levels and health effects, and using fewer acronyms and more graphical representations. Using bullet points, fewer words per sentence, simplifying content and using the CDC's clear communication index (CDC 2014) may help to develop clearer and more comprehensible water quality reports for the public.

To illustrate, the above paragraph has been modified with the above recommendations and presented below. The text before the table has a new reading ease score of 52.5 and a grade level of 7.9:

> All drinking water has at least small amounts of some contaminants. Even bottled water. This does not necessarily mean the water poses a health risk. Some people are more vulnerable to these contaminants than the general population.
>
> They usually have compromised immune systems like
> - Cancer patients undergoing chemotherapy.
> - People with organ transplants.
> - Patients with immune system disorders like HIV/AIDS.
> - Older people and infants can get infections easier.
>
> They should seek advice about drinking water from their health care providers. Otherwise, use the phone numbers below:
>
> IMPORTANT PHONE NUMBERS

Call us for: • Concerns or questions about your water quality • Emergencies	(555) 555-5555 (business hours) OR (888) 888-8888 (emergency/after hours)
EPA's safe drinking water hotline for information on • Water contaminants and potential health effects • Guidelines to reduce infection risk by microbial contaminants (*Cryptosporidium* and others) – ask for a copy • Lead in drinking water, testing methods, and steps to minimize exposure	(800) 426-4791

Bishop (2003) highlights the need to communicate 'negative, unpleasant, or unwelcomed information' to consumers when utilities fail to meet regulations or encounter emergencies (contamination events like the West Virginia chemical spill in January 2014). This is important both during emergencies and in their aftermath in the annual CCR. Being open, ethical, and comprehensible when failing to comply with federal regulations is also essential (Bishop 2003). This should be done while ensuring the readability and understanding are directly addressed using clear, unambiguous statements (e.g., 'tap water not safe to drink' and 'do not drink tap water'). This has the potential to avoid many barriers in communicating risk, especially when CCRs present highly technical information with different possible health outcomes for different subgroups of the population (Berberich 1998). According to Nsiah-Kumi (2008), effective communication is audience-centered, and it is imperative that, in communicating public health messages to communities, we do not neglect vulnerable populations (which includes the linguistically vulnerable). In fact, low literacy is associated with poor health outcomes (Pignone & DeWalt 2006).

When technical information is not effectively rendered for the public, there can be undesirable effects. To illustrate, Wegner & Girasek (2003) found the readability of instruction manuals for child safety seat installation in cars from several manufacturers to be very high; improper use of safety seats is the single strongest risk factor for infant/toddler deaths in traffic accidents (Johnston et al. 1994) and their correct use significantly reduces fatal injury and hospitalization (Kahane 1986). The knowledge gap between experts and the public is wide. So, a good place for water utilities to start is emphasis on identifying what people know at the outset, correcting misinformation, and, subsequently, providing accurate information (Löfstedt & Frewer 1998).

One limitation of the FKR test is that it ignores vocabulary. While readability measurements have some general ability to broadly predict text difficulty, they are not precise, final measures (Pikulski 2002). No mathematical formula can truly measure understanding (Stockmeyer 2009). Future studies on this topic could extend this investigation to evaluate CCRs for cultural appropriateness, the placement of primary messages, and the use of images to reinforce written content using tools such as the simple measure of gobbledygook or SMOG (Wang et al. 2009) and the CDC's clear communication index and risk communication knowledge (World Health Organization 2001). These qualitative and quantitative assessments should be conducted in consultation with seasoned language experts (Oakland & Lane 2004). In addition, there is a need for future research on the benefits of water utility engagement of local residents to act as 'informed partners' in decision-making as pointed out by Glicker (1992).

CONCLUSIONS

Over 300 million residents receive water from a water utility mandated to provide a yearly CCR to its customers (US Environmental Protection Agency 2012) and, hence, the CCR has a large audience. To our knowledge, this is the first study to explicitly examine readability of water quality reports for the US population and it demonstrates that current CCRs are not meeting this standard for a large proportion of the population. Thus, a more

holistic approach is required toward writing these reports, especially, as water utilities move toward electronic delivery (email/online availability) of CCRs (Carpenter & Roberson 2013).

A potential cost-effective suggestion for developing more understandable CCRs is to modify standard US EPA literature in the CCR iWriter software in conjunction with communication and health experts to the NIH recommended 6th–7th grade level. This would involve reducing words per sentence while maintaining text organization and coherence, breaking away from technical jargon, simplifying vocabulary, increasing reliance on pictures/multimedia, usage of active voice, increasing bulleted/numbered lists, using whole numbers for contaminant levels, explaining contaminant violations and health effects, simplifying messages throughout the report, and providing the underlying scientific information with clarity ('water is safe to drink', for instance, should be backed with 'meets/exceeds all federal/state regulations but not necessarily safe for infants/immune-compromised population').

The CCR is potentially a powerful resource for meeting several of the public's health information needs in terms of tap water quality and authentic communication in terms of readability and clarity. The public will have confidence in the safety of the tap water only if the water supplier is trusted (Shovlin & Tanaka 1990). Since consumers use their senses and 'their personal opinions' to assess drinking water (Dietrich 2006), a readable CCR would play a noteworthy role in increasing this trust. Associated goals like increasing awareness of water conservation can also possibly be better achieved. Finally, by addressing the ease of comprehension and reading level of CCRs, water utilities have an excellent chance of influencing population health through informed decision-making on the degree to which tap water can be consumed safely.

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