THE PASSIVATION OF HIGH ENTROPY ALLOYS IN CHLORIDE SOLUTIONS
(Technical Paper)

HOW GOVERNMENTAL INSTITUTIONS HANDLE CORROSION CRISES IN LOW-INCOME COMMUNITIES
(STS Paper)

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On my honor as a University Student, I have neither given nor received unauthorized aid on this assignment as defined by the Honor Guidelines for Thesis-Related Assignments

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The International Measures of Prevention, Application and Economics of Corrosion Technology (IMPACT) study completed by National Association of Corrosion Engineers (NACE) International states that roughly 2.5 trillion USD, 3.4% of the world's gross domestic product, is spent annually on corrosion (2016, para.2). Corrosion has a human cost as well; collapsing infrastructure, aircraft crashes due to corroded parts, and contaminated water all play a part in killing, injuring, and spreading illness among people. Corrosion in the piping and operating equipment of the Union Carbide India Limited pesticide plant in Bhopal, India caused methyl isocyanate gas to leak out of the plant and into the atmosphere. Approximately 800,000 people were exposed to the toxic gas; of those people, 3,800 died immediately (Broughton, 2005, p.1). While the Bhopal incident is a more extreme case, many corrosion related incidents result in deaths and were completely preventable had the proper precautions been taken.

High entropy alloys (HEAs) are a promising solution to the problem of corrosion. These metals made of five or more alloying elements, usually in equimolar amounts, show corrosion-resistance and high hardness and strength when tested on a small scale (Quiambao, 2018, p.1). The technical project will characterize the passivity of five high entropy alloys in order to predict the effects of each alloying element on the properties of the HEA. Ultimately, doing so will lead to the development of a computational method for designing and predicting the properties of novel HEAs. The loosely coupled STS project will focus on local, state, and federal governmental response to corrosion crises, specifically corrosion in water pipelines in lower-class communities.

John Scully, Material Science and Engineering, and his graduate student, Angela Gerard, will oversee the technical project with funding from a U.S. Department of Energy, Office of Science, Basic Energy Sciences grant. Research for the technical project will take place from

June 2019 to May 2020. June through September, potentiodynamic scans of each HEA in sodium chloride solutions of varying pH will be run. September through May, Electrochemical Impedance Spectroscopy (EIS) and X-ray Photon Spectroscopy (XPS) scans will be run to characterize the oxide layers. As EIS and XPS are run, the data will be analyzed and the contributions to passivation properties from each element in the alloy will be determined.

THE PASSIVATION OF HIGH ENTROPY ALLOYS

The technical report will explore the passivation, or the ability of a metal to form a protective oxide layer on its surface which prevents corrosion, of various types of HEAs in varying concentrations of sodium chloride in water (Jones, 1996, p.116). In his 2018 paper published in the Advances in Material Science and Engineering journal, Alvaro Rodriguez, a post-doctorate at the National Energy Laboratory, states that HEAs "are a new group of alloys containing at least five alloying elements with an atomic composition of 5–35% each," and have "high values of mixing entropy" (p.1). However, many HEAs suffer from localized corrosion such as pitting and crevice corrosion because their passive layers are prone to dissolution in the solution to which the metal is exposed (Li, 2019, p.2). According to Pin Lu, a materials design engineer at QuesTek Innovations, the combination of molybdenum (Mo) and tungsten (W) mitigates localized corrosion, although the exact mechanism by which they do so is unknown (2018, p.2). Molybdenum is an element that increases the stability of the HEA's passive layer and, therefore, it will be present in most of the HEAs being tested in this technical research report (Newman, 1985, p.1). The HEAs and binary alloys are all alloyed with some percentage of chromium because chromium increases passivity of the alloy (Quiambao, 2018, p.2). Kathleen Quiambao, a PhD student at the University of Virginia in the Materials Science and Engineering

Department, stated that the oxide layers of alloys with chromium, when analyzed, are found to be chromium rich and result in low current densities in the passive region (2018, p.2).

Corrosion is an essential part of every engineering problem, but often it is overlooked or ignored. In order to save lives and money, engineers must anticipate the potential problems caused by corrosion in their design and adjust the design to mitigate the problems or to keep any failure from injuring people. The most corrosion-resistant HEAs are extremely expensive because they require rare metals like ruthenium (Lu, 2018, p.2). However, these corrosion-resistant HEAs are not required for every application; HEAs that show relatively low passivity, although still higher than that of binary alloys, are often satisfactory for moderately harsh environments and are less expensive than highly passive HEAs. This technical topic will discuss the creation of a computational method for designing HEAs based on their desired properties and then predicting those properties more accurately to speed up the testing process. Figure 1, on page 4, outlines how this will be achieved; characterization tests will determine the properties of several HEAs which will be used to determine how each alloying element contributes to the corrosion properties of the HEA.

The technical objectives include: (1) running polarization scans on various HEAs and binary alloys to determine passivation potentials in salt water and (2) growing and characterizing oxide films on the HEAs' surfaces using EIS and analyzing them using various characterization techniques including XPS and possibly Grazing Incidence X-Ray Diffraction (GIXRD). The process for the creation of a final product is illustrated in Figure 1. While more tests and scans will be performed, Energy Dispersive Spectroscopy (EDS), X-Ray Diffraction (XRD), polarization scans, EIS, and XPS are the most useful in characterizing oxide layers.

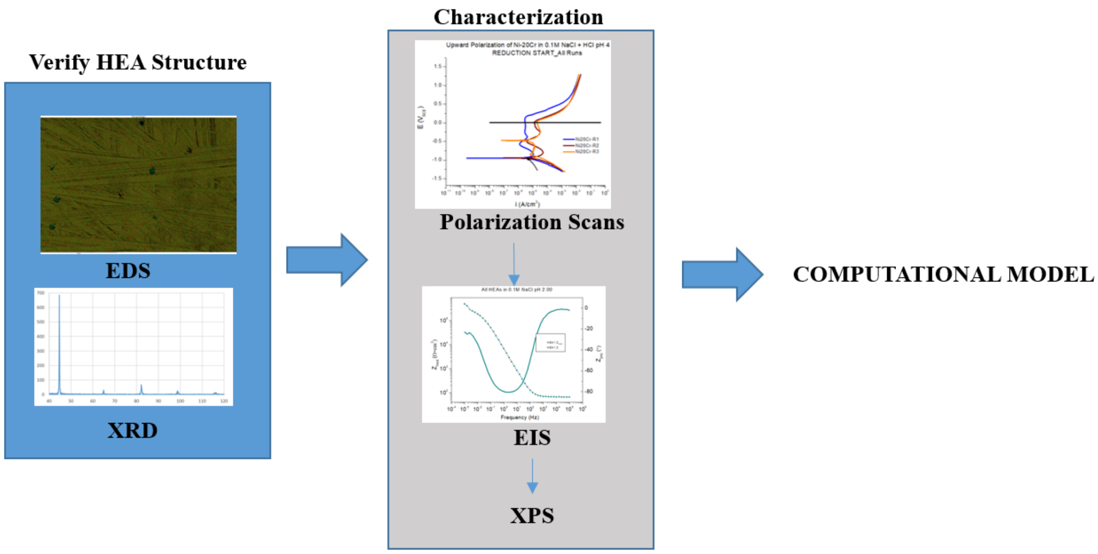

Figure 1: A diagram of the completion of the technical work outlined in the Prospectus. Process of major experiments that will lead up the creation of the computational method. (Teevan-Kamhawi, 2019)

In addition, EDS, XRD, and a variety of other techniques will verify the structure of the binary alloy samples. All of the characterization performed on these HEAs will be compared to the characterization of nickel-, iron-, and cobalt-chromium alloys to understand how each alloying element affects the properties of HEAs. All polarization scans, oxide growths, and EIS will be performed in John Scully's lab (MSB Room 342) and XRD, including GIXRD, and EDS will be run in the instrument rooms (MSB Room 148 and WH Room B003, respectively). The overarching purpose of this project is to develop a computational method for developing new HEAs and predicting their properties based on the alloying elements used. Potential applications for this research includes nuclear waste storage because some of these HEAs show high corrosion resistance in harsh environments. Less passive HEAs can be useful for corrosion prevention in everyday infrastructure; however, they are significantly more expensive to fabricate than conventional alloys. The research paper will be consistent with the guidelines outlined by the Journal of Material Science and the research will be completed over the 2019-2020 school year.

HOW GOVERNMENTAL INSTITUTIONS HANDLE CORROSION CRISES IN LOW-INCOME COMMUNITIES

The lead-contaminated water in Flint, Michigan drew the eye of everyone in the United States to the problem many lower-class, American communities face: failing water-transportation infrastructure. In the early 1900s, state and local governments sanctioned networks of lead pipes to be built for transporting water to homes and buildings within their respective cities (Lewis, 1985). Jack Lewis, Assistant Editor of the Environmental Protection Agency (EPA) Journal, wrote in his 1985 article that the use of lead in pipelines dated back to Roman times and it was chosen because of its “suitability as inexpensive and reliable piping for the vast network plumbing,” although lead was suspected to be toxic at this time, engineers made the decision to use lead due to its toughness (para.5). The problem comes in when water is introduced, especially if that water has corrosive elements in it, such as fluoride and chloride ions (Scott, 2018, p.2). Governmental officials can prevent many of these cases of lead contamination in water by maintaining infrastructure and properly monitoring the lead levels in relevant homes. Unfortunately, even after becoming aware of extraordinarily high lead levels in their cities’ drinking water, officials denied that the water was unsafe and did not allocate tax dollars to finding a solution until the problem developed into a catastrophe (Venkataraman, 2018, pp.8-10).

Flint, Michigan is only one in many cases of water crises due to governmental negligence. Corrosion is often an afterthought for many officials and the people responsible for making decisions about the water treatment process do not assess the consequences of their choices thoroughly. The discovery of corrosion in water pipelines in Newark, New Jersey unfolded similarly to Flint, Michigan (Leyden, 2018a). Officials neglected to inform the public of any problems of which officials were aware and continuously insisted that everything was safe (Leyden, 2018b). According to Liz Leyden (2018b), a reporter for the New York Times:

> For nearly a year and a half after high lead levels were first discovered in the water system, Mayor Ras Baraka and other officials blamed aging lead pipes, insisting on the city's website that the water was "absolutely safe to drink". (p.1)

This quotation raises the questions: how exactly do local governments of a cities affected by corroding pipelines manage the resulting problems? How do the state and federal governments respond? Who else is involved and who has the most power to solve the issues at hand?

The way local governments handle corrosion problems in low-income communities like Newark and Flint can best be portrayed using the STS framework, Technology and Social Relationships, shown in Figure 2, on page 7 (Baritaud, 2009). Local governments, the second most influential group, play a significant role in these crises while the federal government tends to play a smaller role. However, the federal government is responsible for setting and enforcing water quality standards via the EPA. The lack of involvement of the federal government in repairing corroding infrastructure and regulating local governments harms the residents of the affected communities. Advocacy groups tend to provide temporary solutions, such as bottled water, and a voice for affected citizens, but they are unable to provide a permanent solution, like replacing the lead pipes. This permanent solution is the responsibility of the local, state, and federal government because they are employed by the people and to serve the people. News outlets, first local and then national, play an indispensable role in spreading awareness of these problems, specifically that of governmental negligence. They helped to further empower the residents living in these communities; however, the government is still ultimately responsible for finding a permanent solution to the corroding pipelines.

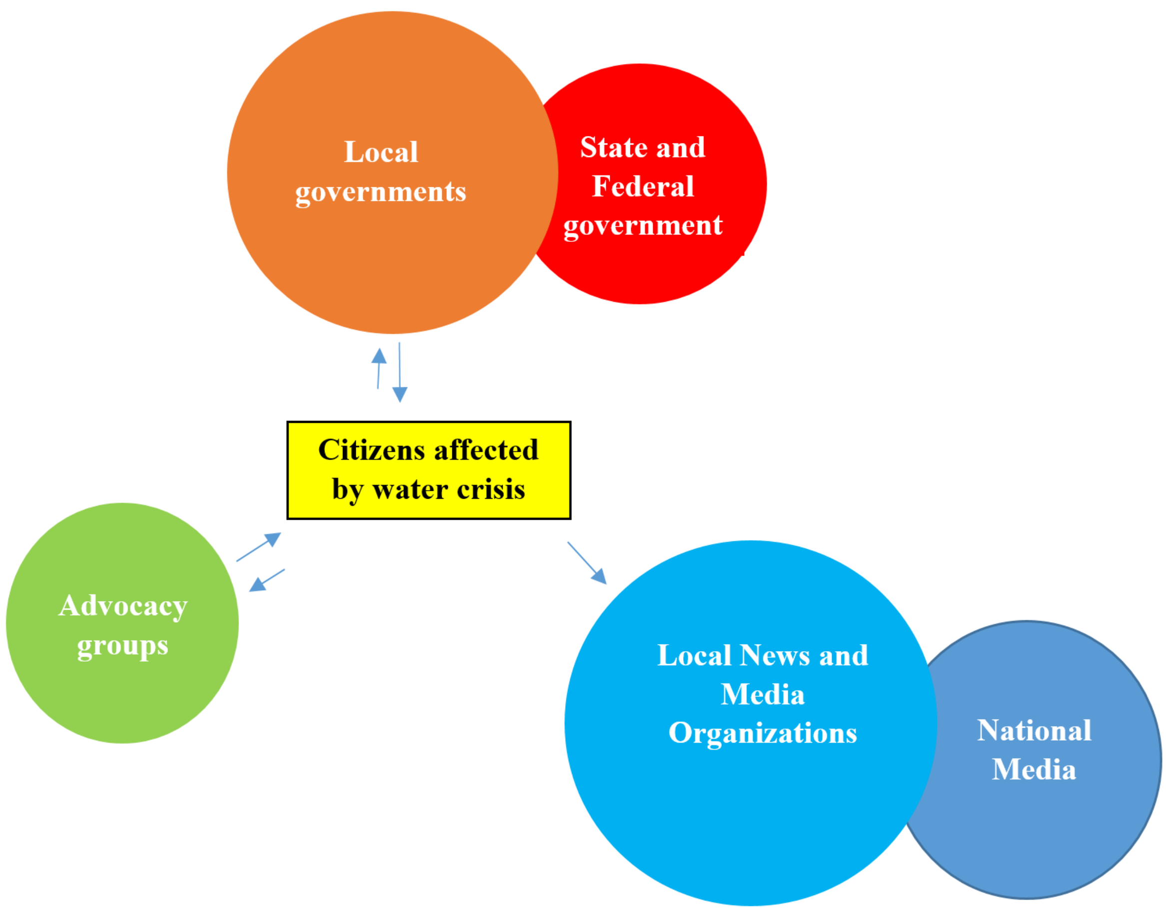

Figure 2: Relationships Between the User and Relevant Groups. This figure shows how the user of the pipelines, the residents of an affected community, interact with the groups involved in the crisis: the government, the news, and advocacy groups. (Teevan-Kamhawi, 2019)

These water pipelines give the government power over the people because this technology is necessary for people to survive. Often, there is not a second option for community members, other than buying expensive bottled water, so the government can charge what it desires for water. When the pipelines began to corrode in both Flint and Newark, releasing large amounts of lead into the drinking water, the local governments still required that people pay their water bills (Leyden, 2018b). While these pipelines were built with lead to increase their longevity, they ended up hurting the user, the residents of the community, because of the actions of the local governments. Advocacy groups further helped mitigate the problem by pointing out the unfairness and inequality the problem presented and by providing resources for the people in the community (Day, 2019, p.359). The engineers responsible for understanding potential failures of and designing the pipelines are not included in Figure 2. This is because, in general, they do not communicate directly to the public. The lack of communication is potentially detrimental to the situation; if community members fully understood the problem and viable solutions, perhaps they would be better suited to push the government for a solution.

These corrosion problems also highlight the issue of infrastructural inequality within the United States, which the STS paper will discuss. Because many of the citizens in cities affected by failing infrastructure are in the lower-class, they often lack the resources to influence government or find alternative solutions when the government is not meeting their needs (Gleason, 2019, pp.412-413). The Actor Network Theory (ANT) is applicable to this situation (Latour, 2005). The actors include: the citizens of the affected areas, the local, state, and federal governments, news and media organizations, engineers and scientists who test the water and who study the causes of the problems, the pipelines themselves, advocacy groups, the Environmental Protection Agency (EPA), and the employees responsible for maintaining water quality standards. The STS paper, will develop the application of ANT to the issue of governmental neglect and discuss potential solutions to corrosion monitoring and reporting in older cities with lead pipelines. A possible solution to the problem can be viewed in Figure 3, which unlike Figure 2, included a line of communication between civil and corrosion engineers and citizens.

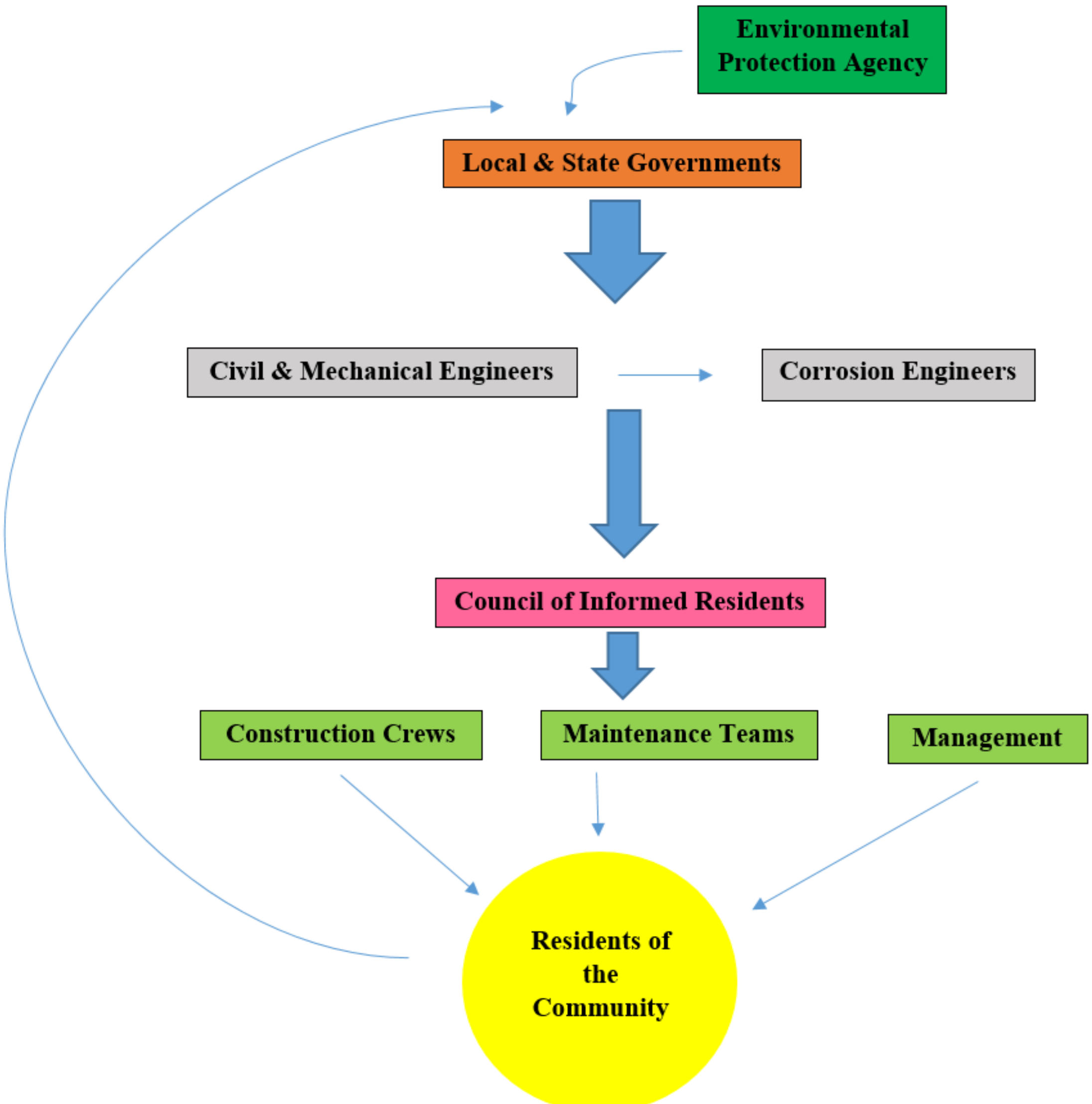

Figure 3: Handoff Framework Diagram Showing How Corrosion-related Problems Should Be Solved. This figure shows the relationship between the actors within the community. (Teevan-Kamhawi, 2019)

The residents of the city and the EPA, who sets standards for the appropriate concentrations of toxic chemicals in water, first notice the problem and consult the local and state governments of the affected community. The governments should then consult civil and corrosion engineers who prototype and test solutions to the problem which is then reviewed by a group of residents who are informed about the issue. The informed residents discuss the ramifications of implementing the solution provided by the engineers and present their findings to the local government. The local government should then decide the best course of action and employ the workers needed to solve the problem for the local community. The problem people in these lower-income communities face is the engineering and discussion steps are missing from the process when the local government attempts to find solutions. This will provide lines of communication between residents, and the local government and engineers. Doing so will increase the power of the residents to choose a solution, rather than the local government bearing all of the responsibility to do so.

The STS and loosely coupled technical reports will both explore the dangers and consequences of corrosion. The STS paper will focus on infrastructural inequality and the gap engineers tend to have in their consideration for corrosion when designing infrastructure. The technical report will explain and discuss a technology which can be used to reduce the dangers of corrosion in infrastructure and other technologies.

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