SUPER-CHARGED PULSED JET COMBUSTOR FOR SALT-WATER SEPARATION
IN REMEDIATING HYDRO FRACTURING BRINES

A Thesis in
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by
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ABSTRACT

Historically, petroleum production processes (*e.g.*, oil, natural gas, and coal extraction) have produced briny wastewater streams, with total dissolved solids concentrations near saturation. Presently, the unprecedented production of natural gas from deep, low-permeability, sedimentary rock formations within the continental United States (particularly the northeast) has brought heightened scrutiny to oil and gas well stimulation (*i.e.*, through the hydraulic fracturing process). Of particular environmental concern is the collection, transportation, storage and ultimate fate of the hypersaline wastewaters from natural gas wells.

Natural gas production wells that have been stimulated by hydraulic fracturing release nearly half of the three to five million gallons of fluid used in the process. This mildly saline water is called flowback. Although flowback lasts for only a few weeks, for the remainder of its lifetime the well will produce a more saline wastewater called produced brine. The chemical composition of these wastewaters is complicated, as they contain significant concentrations of organic molecules and radioactive isotopes. Because the solids content can be over 20% the total solution mass, traditional wet chemistry and conventional desalination techniques (*e.g.*, reverse osmosis, thermal distillation, etc.) are ineffective for remediating these wastewaters. This has led to deep well reinjection to become the sole disposal option for these wastewaters.

In this thesis, an unconventional remediation technique for these hypersaline brines is investigated. Since the main contaminant in flowback and produced brines is a high concentration of dissolved solids, the author employed surrogate hypersaline brines that were artificially created and experimentally remediated by using a proprietary super-charged pulsed jet combustor technology.
In this research, the super-charged pulsed jet combustor was investigated as a potential technology for separating the salt from water, in solutions near saturation (with respect to sodium chloride). Pulsating combustors are known for their exceptional fuel efficiency, as well as their ability to produce powerfully turbulent exhaust fields, which enhance convective drying rates. In this thesis, the experimental, pilot-scale system used was capable of processing brines with total dissolved solids concentrations above 200,000 mg/L – meeting a current technology gap in the field of flowback and produced brine treatment. It demonstrated the ability to evaporate nearly one-third the solvent mass of a nearly 0.5 gallons per minute (114 liters per hour) hypersaline brine flow, while retaining almost all the mass of processed solids within a five foot (1.52 meter) diameter round basin located beneath the tailpipe end of the combustor.
# TABLE OF CONTENTS

LIST OF FIGURES ...................................................................................................................... viii
LIST OF TABLES ........................................................................................................................ xii
UNITS AND NOMENCLATURE ............................................................................................... xiii
ACRONYMS AND ABBREVIATIONS ......................................................................................... xiv
ACKNOWLEDGEMENTS ........................................................................................................... xv

## CHAPTER 1: INTRODUCTION ................................................................................................. 1

1.1 What is Hydraulic Fracturing? ........................................................................................... 1
1.2 The History of Hydraulic Fracturing ............................................................................... 1
1.3 The Process of Hydraulic Fracturing ............................................................................... 3
1.4 The Benefits of Natural Gas ............................................................................................. 5
1.5 Natural Gas Markets and Economies ................................................................................ 11
1.6 Environmental Concerns ................................................................................................. 15
1.7 Summary .......................................................................................................................... 22
1.8 References ....................................................................................................................... 24

## CHAPTER 2: BACKGROUND ............................................................................................... 31

2.1 Using and Producing Water ............................................................................................. 31
2.2 Contamination .................................................................................................................. 38
2.3 Past Wastewater Disposal Options ................................................................................ 45
2.4 Current Wastewater Fate ................................................................................................. 46
2.5 Conventional Wastewater Treatment Options ............................................................... 49
2.6 Unconventional Wastewater Treatment Options ........................................................... 62
2.7 Summary .......................................................................................................................... 63
2.8 References ....................................................................................................................... 64

## CHAPTER 3: LITERATURE REVIEW .................................................................................... 72

3.1 Introduction ....................................................................................................................... 72
3.2 Pulsating Combustors: Pulsed and Pulse Combustors .................................................... 73
3.3 The History of Pulsating Combustors .............................................................................. 78
3.4 Common Applications of Pulsating Combustors ............................................................. 79
3.5 Drying .................................................................................................................. 80
3.6 Spray Drying ......................................................................................................... 81
3.7 Atomization ........................................................................................................... 83
3.8 Pulsating Combustors as Dryers .......................................................................... 86
3.9 Summary ............................................................................................................... 107
3.10 References .......................................................................................................... 108

CHAPTER 4: THESIS OBJECTIVES ........................................................................... 115
4.1 Project Introduction .............................................................................................. 115
4.2 Thesis Objectives ................................................................................................ 116
4.3 Thesis Format ....................................................................................................... 116
4.4 References ............................................................................................................ 119

CHAPTER 5: TESTING AND EVALUATING THE PROCESS ..................................... 120
5.1 Introduction .......................................................................................................... 120
5.2 Materials .............................................................................................................. 120
5.3 Experimental Methods ....................................................................................... 124
5.5 Discussion ............................................................................................................ 132
5.6 Chapter Summary ............................................................................................... 140
5.7 References .......................................................................................................... 142

CHAPTER 6: THERMODYNAMIC SYSTEM ANALYSIS ......................................... 143
6.1 Introduction .......................................................................................................... 143
6.2 Materials .............................................................................................................. 144
6.3 Methods ............................................................................................................... 144
6.4 Results & Discussion ......................................................................................... 149
6.5 Summary ............................................................................................................. 159
6.6 References .......................................................................................................... 160

CHAPTER 7: TESTING THE SYSTEM USING A NOVEL SCREEN ARRAY ............. 161
7.1 Introduction .......................................................................................................... 161
7.2 Materials & Methods ......................................................................................... 161
7.3 Results ................................................................................................................ 163
7.4 Discussion ........................................................................................................... 167
7.5 Summary ............................................................................................................. 170
CHAPTER 8: CLOSING STATEMENTS ........................................................................... 172

8.1 Project Summary .................................................................................................. 172
8.2 Future Research Investigations ............................................................................. 172
8.3 The Potential to Treat Other Brines .................................................................... 181
8.4 Full-Scale Considerations .................................................................................... 182
8.5 Summary ............................................................................................................... 184
8.6 References ............................................................................................................ 185

APPENDIX A ............................................................................................................... 188
APPENDIX B ............................................................................................................... 225
APPENDIX C ............................................................................................................... 230
LIST OF FIGURES

Figure 1.1  A graphical depiction of a horizontal, hydraulically fractured, natural gas extraction well............................................................................................................4
Figure 1.2  The calculated ratios of the heat accumulated due to the greenhouse gases (GHGs) emitted from both lifecycle and pure combustion of bituminous coal, diesel oil, and natural gas to the heat resulting from their combustion.........................................................7
Figure 1.3  Shale gas plays in the continental U.S.........................................................................................................................9
Figure 1.4  The proved natural gas shale reserves of the top six producing states, from 2009-2013 .........................................................................................10
Figure 1.5  U.S. natural gas gross imports and exports, and net imports, from 1973-2011 .............................................................................................................11
Figure 1.6  The fluctuating price of natural gas, as shown by Henry Hub Spot Prices................................................................................................................................14
Figure 1.7  Comparison of carbon emissions per amount of energy consumed, for shale and conventional gas, coal, and diesel oil. Estimates are for a 100-year time horizon.....................................................................................19
Figure 2.1  The risks posed by hydraulic fracturing to water resources, divided by phases of natural gas production ...........................................................................31
Figure 2.2  Concentration versus time for a few selected properties; measured by the PADEP Bureau of Oil & Gas Management (BOGM) for Bosnall 7 well in Clearfield, PA, sampled in Oct. 2008..........42
Figure 2.3  Data from a 2013 study by Barbot, et al., showing increasing TDS concentration with time for flowback from three Marcellus Shale well sites in PA. Site A was fractured using reused flowback compared to freshwater used at sites B1 and B2........48
Figure 2.4  A conventional, multi effect distillation, sea water desalination unit ......... 55
Figure 2.5  The dewevaporation process..............................................................................................................................56
Figure 2.6  An Aqua-Pure mechanical vapor recompression NOMAD unit.............. 59
Figure 2.7  Conventional membrane process shown at left, compared to the Vibratory Shear Enhanced Process, which prevents flux loss due to membrane plugging..............................62
Figure 3.1  A mechanically-valved (spring-loaded, flapper-type valves) pulse combustor versus an aerovalved (or valveless) pulse combustor.......................... 74
Figure 3.2  One pulse combustion cycle as shown in four phases.......................... 75
Figure 3.3  The V-1 flying bomb; once launched, it was propelled by the Argus As 014 pulse jet ................................................................. 78
Figure 3.4  The Hosokawa Bepex Corp. 80-150 Hz, 300 kW rotary-valved, pulse combustor drying system ................................................................. 79
Figure 3.5  A mobile unit produced by Pulse Drying Systems, Inc., for recovering valuable minerals from wastewater................................. 80
Figure 3.6  A typical spray drying process layout .............................................................. 81
Figure 3.7  Droplet break up characterized by Weber (We) number range ............. 85
Figure 3.8  Within the exhaust from pulse combustion, the insulating surface boundary layer is stripped in one direction then a very short time later, to the other (to the right); and this constant oscillation continues........................................................................................................90

Figure 3.9  From Ain, et. al., where 1 represents air flow velocity = 4 m/s, 2 = 6 m/s, 3 = 8 m/s, \( \tau \) represents total droplet evaporation time (in seconds), and \( f \) = air pulsation frequency in Hz (s\(^{-1}\))..............................90

Figure 3.10  Nusselt number, gas temperature, and heat flux along tailpipe axial length. For (a) flow is nonpulsating; for (b) it is pulsating at 83 Hz. Tailpipe length is equal for both conditions. Note the significantly larger Nusselt numbers in case (b)......................................................91

Figure 3.11  Sound intensity versus input power for a flapper-valved pulse combustor......95

Figure 3.12  The calculated NO generation rate along the x-axis of Keller and Hongo’s pulse combustor, for pulsing and nonpulsing conditions.................99

Figure 3.13  The spray dryer used by Wu and Liu that uses a pulsating combustor...........102

Figure 3.14  Combustion chamber pressure oscillations. There are several noted changes between both conditions; not noted is that in condition (a) the volume of the combustor chamber is 1,000 cm\(^3\); whereas in (b) it is 400 cm\(^3\). According to the source, the primary purpose in comparing and contrasting these plots is to show the “non-optimal point of combustor performance” (a) versus the “optimal point of combustor performance.” Because a the combustor had a “conical-cylindrical combustion chamber” and the combustor tailpipe length is identical for each condition shown, it is possible that this was a pulse combustor, where combustion frequency and air and fuel flow rate were uncontrollable, and the difference in body geometry between the two conditions shown is primarily responsible for all the observed differences – most notably the shape and amplitude of the pressure oscillations.................................................................105

Figure 5.1  An example of the fluid heat exchanger around the combustor body, showing the flow direction of the fluid, and the exhaust from the combustor. Drawing is not to scale. View is from directly above the combustor, which is shown sitting on its stand..................122

Figure 5.2  A process flow diagram for the control and operation of the super-charged, pulsed jet combustor. Data/control signals are shown as large, dashed lines. Electrical current from the rotating valve to the spark plug is shown by a small, dashed line. Not to scale.................................................................125

Figure 5.3  The “goose-neck” or “down spout” or injector.............................................125

Figure 5.4  The mass fractioning and mass determination process. Mass collected in the plastic basin is physically segregated and categorized as being either mostly liquid or mostly solid. It is subsequently divided into completely solid and liquid mass amounts, by the methods shown.................................................................126
Figure 5.5 The mass of water collected in the pool as a percentage of the total water mass processed through the system for brine and tap water tests...

Figure 5.6 Linear trendline fits for the experimental data in the flow range between the 0.17-0.48 gpm (0.011-0.03 kg/s) range of water flow rates through the system. Solid line is the linear trendline fit for the brine data. Dashed line is the linear trendline fit for the tap water data...

Figure 5.7 The mass of salt collected in the plastic basin after each experiment, reported as a percentage of the total salt that was in the brine.

Figure 5.8 The raw data of meteorological conditions (i.e., ambient outdoor temperature and relative humidity) and the percent water vaporization results for each of the thirteen tests conducted over seven days. Based on the raw data no discernable relationship seems to exist.

Figure 5.9 The remaining water vapor capacity of air ($x_v$) versus the average percentage of water mass vaporized by the supercharged pulsed jet combustor, on the date of each experiment. The direct relationship between water flow rate through the system and the percentage of water vaporized is accounted for by multiplying the water mass flow rate through the system by the percentage of water mass vaporized by the system.

Figure 6.1 The front-end-coil array without thermocouples installed.

Figure 6.2 The front end coil array in place.

Figure 6.3 Process locations where the temperature (“t”) of the water data was recorded.

Figure 6.4 Down spout positions relative to the combustor’s exhaust end. Not to scale. (a) Shows the down spout position when water was injected into the combustor’s exhaust. (b) Shows the down spout rotated 180° degrees, such that water is still ejected through the pipe end, but out of the combustor’s exhaust.

Figure 6.5 A top view of the general experimental set up, where water is ejected down into the combustor’s exhaust gas, and whatever is not vaporized is collected in the large plastic basin on the ground.

Figure 6.6 Power efficiency (as measured against total system power) of each energy-recovery section (i.e., heat exchanger and front-end-coil array). Note that the front-end-coil array does not recover more power, when the water flow through the system equals 0.16 kg/s (2.57 gpm) while the heat exchanger around the combustor body does.

Figure 6.7 Percentages of water mass recovered based on the orientation of the down spout injector (i.e., directed such that water was injected into the combustor’s exhaust or out of and away from the exhaust).

Figure 7.1 Top view of the combustor and screen set up, with liquid atomizing in the hot, exhaust gas stream. Not to scale.

Figure 7.2 The left-hand-side screens and plate array in place, with the duck bill injector.
Figure 7.3  An image depicting the naming convention used for the left-hand-side screens, which collected salt. A separation between the two screen pieces is shown and exaggerated for clarity. Not to scale........ 164

Figure 4  The amount of salt on each of the two left-hand side screens, as a percentage of the total salt collected across both screens. The top figure shows the experiments in order of increasing fuel flow to the combustor (units of g/s; left to right). The bottom shows the experiments in order of increasing brine flow rate (units of kg/s; left to right). Test number and date are shown beneath each column........................................................................................................ 165

Figure 7.5  Hydrated salt paste on screens after tests. (a) Near screen, test #2 on June 4th, 14.5 grams of salt (dry). (b) Near screen, test #1 on June 10th, 69.4 grams of salt (dry); this hydrated paste had the appearance and consistency of shaving cream. Note that the backing plate has been removed prior to taking these photographs........................................................................................................ 166

Figure 7.6  The percent of total salt mass processed during a run which was collected onto both left-hand side screens at different brine flowrates and different fuel (propane) flow rates. Data is segregated by average fuel mass flow rates.................................................................................. 168

Figure 7.7  Although there may be a trend, there does not appear to be a significant linear relationship between increasing the fuel flow rate to the combustor and the subsequent increase in the percent of salt mass collected on the screens.......................................................................................... 169

Figure 7.8  Salt deposits that were observed but not collected after experiments. (a) shows salt encrusted on the pipe end that was shaped like a duck bill. (b) shows hydrated salt paste that has plastered the plate that backed the screens and a plastic clamp. (c) shows a film of salt that covers some of the end of the combustor’s tailpipe. Considering the small masses of salt collected on the screens (20-100 g), these amounts (especially those shown in (a) and (b)) may have been significant................................................................. 171

Figure 8.1  A view of the Unison Drying System, by Bepex, atomizing a 1 gpm (227 lph) liquid feed without a nozzle........................................................................................................ 176

Figure 8.2  The relationship between particle entrainment factor (η) and combustor oscillation frequencies..................................................................................................................... 177

Figure 8.3  Four cases of Rayleigh’s criterion, where the amplitude or phase angle of normal combustion chamber pressure (solid line) is altered (the result being shown by the dashed line) by instantaneous energy release (Q) at critical points. Case 1 represents the condition where resonant pressure amplitude is increased by instantaneous energy addition at the correct times, while in Case 2, adding it at the wrong time decreases amplitude.......................................................................................... 180
LIST OF TABLES

Table 1.1  The chemical composition of raw natural gas, LNG, and LPG..............................7
Table 1.2  Pennsylvania business sectors and direct and indirect revenue from Marcellus Shale industry, during 2010, in millions of U.S. dollars.................................................................................................................................13
Table 1.3  Properties of compressed and liquefied natural gas........................................19
Table 1.4  A brief summary table listing the pros and cons of shale gas production.........23
Table 2.1  Commonly encountered concentrations for major, reoccurring constituents of flowback and produced brine wastewaters emanating from natural gas wells in the Marcellus Shale gas play. The “single well” columns are for the same well. “Early” and “late” refer to time after well completion........41
Table 2.2  Waste generated in PA during 2011 from the Marcellus Shale gas play...........47
Table 2.3  Desalination process applicability based on influent feed TDS concentration.....63
Table 3.1  Typical evaporative capacity and energy consumption (kJ/kg of water evaporated) for pulse combustion dyers and other conventional dryers.............98
Table 5.1  The thirteen tests conducted to determine the super-charged pulsed jet combustor’s salt-water separation properties at different salinities and brine flow rates.................................................................128
Table 5.2  Solid (i.e., salt) and liquid water masses across the process..............................130
Table 5.3  Detailed outdoor ambient and humidity capacity results for each test date, yielding $x_s$ and $x_c$. Also included is the average percent of water vaporized corrected for its relationship to water flow rate through the system..................139
Table 6.1  Temperature and power (recovered through conductive thermal energy transfer) results from the four front-end-coil tests..........................................................150
Table 6.2  Combustor power and total system power recovery (through conductive thermal energy transfer) results from the four front-end-coil tests........152
Table 6.3  Water temperature and mass balances for the directional down spout experiments. Influent refers to the water temperature prior to the heat exchanger around the body; while effluent refers to the water temperature after the body heat exchanger but before discharge through the down spout......155
Table 6.4  System thermodynamic analysis........................................................................157
Table 7.1  Results of salt-on-screen collection tests at Penn State..................................164
Table 7.2  The effect of increasing fuel flow rate on salt collection onto the screens........169
Table 8.1  Effects of air-fuel ratio on pulse combustion and instantaneous thrust in a pulse jet..............................................................................................................................174
UNITS AND NOMENCLATURE

Δ  change
°  degree
bbl  barrel (42 gallons)
BTU  British Thermal Units
C  Celcius
cfm  cubic feet per minute
Ci  Curie
cp  specific heat
d  day
dB  decibel
F  Farenheit
ft  foot
g  gram
gal  gallon
gpm  gallon per minute
H  enthalpy
HP  horse power
hr  hour
Hz  Hertz
in  inch
J  Joule
K  Kelvin
kg/s  kilograms per second
kWh  kilowatt hours
L  liter
lph  liter per hour
lpm  liter per minute
lps  liter per second
lb  pound
m  meter
min  minute
MMBTU  one million British Thermal Units
P  Poise
Pa  Pascals
pH  acidity or basicity of solution
φ  equivalence ratio
ppm  parts per million (sometimes mg/L)
psi  pounds (force) per square inch
R²  coefficient of determination
ρ  density
s  second
SCFM  standard cubic feet per minute
T  temperature
W  Watt
## ACRONYMS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>Inc</td>
<td>Incorporated</td>
</tr>
<tr>
<td>LLC</td>
<td>Limited Liability Company</td>
</tr>
<tr>
<td>PADEP</td>
<td>Pennsylvania Department of Environmental Protection</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids</td>
</tr>
<tr>
<td>U.S.</td>
<td>United States</td>
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<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
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CHAPTER 1: INTRODUCTION

1.1 What is Hydraulic Fracturing?

Hydraulic fracturing is a well-stimulation technique used to release deposits of natural gas trapped in impermeable, horizontal lenses of sedimentary rock (particularly shale) thousands of feet beneath the surface of the Earth. By artificially creating zones of high permeability around a wellbore, the formerly confined natural gas flows freely to the surface. These porous extraction zones are formed using pressurized water to crack the sedimentary rock reservoir, and then filling these fractures with a sand or ceramic slurry, to keep them from closing [1, 2].

1.2 The History of Hydraulic Fracturing

Although humans have known about surface emissions of natural gas since ancient times, the first recorded use of the gaseous, hydrocarbon mixture was by the Chinese around 500 BC, who used it to thermally desalinate water [2, 3]. The use of natural gas by humans continued, and by the end of the 18th century, Britons were using an artificial substitute made from coal to power the lamps in their cities – a practice which quickly spread across the Atlantic to the U.S. [3]. By the end of the 19th century, the U.S. embarked on the lengthy project of building and installing natural gas transportation [2, 3]. Completed in the 1960s, this infrastructure investment has provided the U.S. a network through which to distribute newly produced shale gas.

Throughout the 20th century, the primary use of natural gas was to generate electricity [3]. In 1978 during the Carter U.S. presidential administration, however, the Powerplant and Industrial Fuel Use Act was passed, which all but banned using natural gas in U.S. powerplants
Ultimately in 1987 the law was repealed, and ever since demand for natural gas has steadily risen [4, 5].

Although geologists knew for decades about the hydrocarbon-rich, sedimentary reservoirs deep beneath the United States, the oil and gas industry could not economically recover it until recently [3, 5-7]. The first use of hydraulic fracturing was in the 1940s, when it replaced the well stimulation technique of blasting with nitroglycerine charges, which was used to extend the production life of oil wells [3]. By the 1970s, hydraulic fracturing became a common practice in the tight gas sands of the western U.S. [1]. Beginning in 1982, George Mitchell (founder of the Mitchell Energy and Development Corporation) began experimenting with hydraulic fracturing in the Barnett Shale Formation, in Texas, but did not see significant success until 1998 [3]. Although the Barnett play is now on the decline, techniques and lessons learned by George Mitchell in Texas serve as the foundation for modern hydraulic fracturing [3, 6].

Historically, natural gas sources were co-developed with crude oil production wells [6]. Because gaseous hydrocarbon freely flowed from these reservoirs into wellbores, they were referred to as “conventional” sources [7]. In contrast, the recently-exploited, impermeable, sedimentary reservoirs are commonly called “unconventional resources” [1, 3, 6, 8]. These trapped hydrocarbon deposits can be further segregated into the categories: shale gas and oil, tight gas and oil, and coal bed methane or coal bed gas [3, 6, 8, 9]. Since both the terms “shale gas reservoir” and “tight gas reservoir” refer to low-permeability, sedimentary rock formations

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1 In 1969, an atomic bomb detonation in Colorado was tested as a method of releasing trapped natural gas [15]! Though it worked, the gas was deemed too radioactive for use, and the site had to be remediated.
2 A commonly used term that refers to a zone of low-permeability.
which contain significant deposits of natural gas, no further distinction is made between them in this paper.

Previously, unconventional resources were both unreachable and not economically viable production sources. Because shale gas deposits exist as in horizontal, subterranean lenses, to effectively tap these resources a vertical extraction wellbore must be turned 90°, maximizing contact with the reservoir [1, 6]. The problem of turning a well from the vertical to horizontal plane was solved in the 80’s and 90’s, with the development of rotary steerable drilling systems [1, 10]. Simultaneously, the industry has perfected another technological requirement necessary to access unconventional reservoirs: the ability to determine their exact location while still on the Earth’s surface [3]. With both of these issues resolved, hydraulic fracturing in horizontal wells has become standard practice, and this combination has unlocked the sedimentary, hydrocarbon reservoirs of both the United States and the world [3]. With a $20 billion annual activity in 2012, hydraulic fracturing – the process making the shale gas boom possible – has been hailed by petroleum production experts as, “[O]ne of the most important new, activities of the petroleum industry” [1].

1.3 The Process of Hydraulic Fracturing

Once petroleum engineers and geologists have determined the location and depth of a shale gas reservoir, drillers spud a well on the Earth’s surface above the geologic formation. Advanced and directionally controlled by a drilling rig on the surface, a drill bit creates a vertical wellbore. As the bit bores through the Earth’s crust, steel casing follows behind it to prevent cave-ins and to give shape to the wellbore [3]. To keep the casing in place, cement is injected into the annulus (i.e., the empty space between the ground and the outside of the well casing) [3].
At a predetermined depth, the drilling rig turns the drill bit from the vertical to the horizontal plane. This 90° turn is formed by advancing the bit simultaneously in both the vertical and horizontal directions, over a vertical distance of about 1,000 feet (305 m) [3].

Once the well is completed and cleaned, hydraulic fracturing can commence. This proceeds in sequence of distinct stages [1, 6]. First, pad\(^3\) is injected at a pressure above the “breakdown pressure” of the formation (usually 7,000 – 10,000 psi; 48,000 – 68,000 kPa), causing tensile failure of the rock, creating fissures [1]. As more fluid is injected, cracks (<0.25” [0.635 cm] wide) continue to propagate – some to a length of 3,000 feet (914 m) [1, 11].

\(^3\) Another term for fracturing fluid used during the hydraulic fracturing well-stimulation technique.

Figure 1.1 A graphical depiction of a horizontal, hydraulically fractured, natural gas extraction well [63].
The goal of well stimulation, however, is not to create millions of fractures in random locations along the wellbore. Rather, operators use well completion methods to selectively target specific locations in gas-laden formation.

There are three common hydraulic fracturing well completion techniques: open hole; open hole with liners and sleeves for multiple zones; and perforation (often shortened to “perf”) and plug [1]. Open hole is the most rudimentary and does not control the location where fracturing occurs. The open hole with liners and sleeves method uses (usually inflatable) barriers to isolate certain regions of the wellbore, and only hydraulically fracture within these. The perf and plug technique relies on a remote-controlled gun to deliberately puncture the well casing at chosen locations, and then, like the liners and sleeves method, gelatinous plugs are deployed to segregate these punctured wellbore portions for subsequent fracturing.

After the pad fractures the formation surrounding the wellbore, proppant is injected [1]. True to its name, proppant is a sand slurry which “props” the fissures open, preventing the overburden formation pressure from closing off the cracks when the fluid is withdrawn [3]. After injecting the proppant slurry into the well, an overflush forces the aggregate into the fractures [1]. The well is now ready for production.

1.4 The Benefits of Natural Gas

Regardless of the technological advances, locating and extracting natural gas from impermeable rock formations is undeniably complicated and costly. Just drilling and fracturing a well can cost up to five million dollars, and completing the last 10% of the well length represents 50% of the total cost [12]. With such a high price tag, what factors make the development of unconventional natural gas resources worth the cost?
1.4.1 Cleanliness

Natural gas is said to be the cleanest burning fossil fuel, emitting less SO\textsubscript{2}, CO, NO\textsubscript{x}, and CO\textsubscript{2} (the latter two being greenhouse gases [GHGs]) than other commonly used liquid or solid hydrocarbon fuels [3, 9, 10, 13]. Per energy unit, natural gas combustion emits 45\% less CO\textsubscript{2} than coal, 30\% less than oil, and 20\% less than gasoline [2, 9]. A brief 2013 study by Roger Sathre, found that the lifecycle (i.e., including extraction, processing, and transportation) greenhouse gas emissions for natural gas were significantly lower than those for coal and diesel oil, as shown in Figure 1.2 [14]. Although there is some debate about the true lifecycle greenhouse gas emissions from natural gas use and production, there seems to be widespread agreement that natural gas releases less greenhouse gas than coal [7, 15].

Despite the laud heaped on natural gas, it is a fossil fuel. As shown in Table 1.1, raw natural gas and its refined products are gaseous mixtures of methane (CH\textsubscript{4}), ethane (C\textsubscript{2}H\textsubscript{6}), propane (C\textsubscript{3}H\textsubscript{8}), and butane (C\textsubscript{4}H\textsubscript{10}) hydrocarbons, as well as minor amounts of impurities (e.g., carbon dioxide, hydrogen sulfide, and nitrogen gases and water) [2, 3, 10]. Consequently, many environmentalists consider it only a “bridge fuel” – a marginally “cleaner,” petrochemical fuel that can power the quest for renewable energy sources [6]
Figure 1.2 The calculated ratios of the heat accumulated due to the greenhouse gases (GHGs) emitted from both lifecycle and pure combustion of bituminous coal, diesel oil, and natural gas to the heat resulting from their combustion. Adapted from [14].

Table 1.1 The chemical composition of raw natural gas, LNG, and LPG [2].

<table>
<thead>
<tr>
<th></th>
<th>Natural Gas</th>
<th>LNG&lt;sup&gt;1&lt;/sup&gt;</th>
<th>LPG&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>81.20 - 86.70</td>
<td>70.00 - 87.20</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>2.90 - 8.50</td>
<td>8.61 - 15.00</td>
<td>2.2</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td>1.70 - 2.74</td>
<td>2.74 - 10.00</td>
<td>97.3</td>
</tr>
<tr>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>0.14 - 0.71</td>
<td>1.07 - 3.50</td>
<td>0.5</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.87 - 1.80</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.60 - 14.40</td>
<td>0.36 - 0.90</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>1</sup>Liquefied natural gas (LNG)

<sup>2</sup>Liquefied propane gas (LPG)
1.4.2 Potential for Energy Independence

For decades, Americans have lamented their dependence on foreign oil. The enormous deposits of natural gas trapped beneath the wealthy but resource-stressed U.S. offer the potential of national energy independence [15]. In 2000, an optimistic but unproved estimate claimed that the U.S. has over 780 trillion ft\(^3\) (22.1 trillion m\(^3\)) of conventional and unconventional natural gas sources [3]. Figures published in August 2013 were a bit more conservative, asserting that the United States had 348.8 trillion ft\(^3\) (9.9 trillion m\(^3\)) in proved reserves of wet\(^4\) natural gas [16]. Regardless of disparities between volume estimates, the supply of natural gas in the U.S. is considered very reliable [12].

Despite the massive shale gas deposits beneath the United States, this country has only 4.1% of the total proved natural gas reserves in the world [3]. At 1,688 trillion ft\(^3\) (47.8 trillion m\(^3\)), Russia is believed to have the most shale gas [2, 6, 17]. Additionally, many countries remain relatively unexplored, compared to the United States; and these may also hold massive unconventional natural gas deposits [3]. Nonetheless, the U.S. is the undisputed leader in shale gas development, and led in world production during 2013 [6]. And there is no end in sight:

Natural gas production in the U.S. is expected to continue to rise in the coming decades. Presently there are over 20 shale oil and gas plays\(^5\) in the U.S. [18]. As shown in Figure 1.3, they are located throughout the country. Of these, seven are recognized as the nation’s top shale gas plays: the Barnett, Haynesville, Fayetteville, Woodford, Bakken, Eagle Ford, and Marcellus [19]. With 33 trillion ft\(^3\) (0.93 trillion m\(^3\)) proved reserves, prior to 2012, the Barnett Shale in TX was the largest and most developed shale gas play in the United States [16, 20]. Since then,

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\(^4\)“Wet” natural gas contains heavier hydrocarbons (i.e., ethane, propane, butane, and pentane) plus water and other impurities, while “dry” natural gas is almost entirely (~ 90%) methane and is less valuable [4, 8].

\(^5\) A “play” refers to a particular geologic field [8].
however, the Marcellus Shale gas play underneath PA, OH, NY and WV has exceeded the Barnett, becoming the undisputed leading shale gas play in the nation [21, 22].

In 2005, hydraulic fracturing came to the U.S. eastern coast, with Range Resources drilling and fracturing the first horizontal, shale gas well in the Marcellus Shale play [23]. This massive Devonian reservoir lies beneath the states of Pennsylvania, Ohio, West Virginia, and New York. With estimates claiming it has enough gas to power the U.S. for the next 45 years, the Marcellus Shale is a major natural gas field in the United States [3, 5, 6, 24]. Additionally, the still-developing Utica Shale gas play lies several thousand feet beneath the Marcellus Shale,

Figure 1.3 Shale gas plays in the continental U.S. [64].
and based on 2012-2013 estimates it is expected to hold seven times more crude oil but only about half the volume of shale gas as the Marcellus Shale formation [3, 22, 25, 26].

The Marcellus Shale gas play is extremely important not only due to its large volume, but also because it is geographically located near the eastern coast of the U.S. – a huge natural gas market [19]. Of the four states which cover the tight gas play, Pennsylvania has emerged as the leader in natural gas production [1]. Due to Marcellus Shale gas production, between 2011 and 2012, Pennsylvania jumped from seventh to third largest producer of natural gas in the U.S, and by 2013 would be the second-largest producer [27].

![Figure 1.4](image-url)  
Figure 1.4 The proved natural gas shale reserves of the top six producing states, from 2009-2013 [22].
**1.5 Natural Gas Markets and Economies**

Birthed by rising natural gas prices and horizontal drilling and hydraulic fracturing technologies simultaneously coming of age, the U.S. shale gas boom could not have come at a more opportune time [20]. The 2008 collapse of the inflated U.S. housing market plunged the country into an economic recession [28]. At the time, the U.S. was a major importer of natural gas. As shown in Figure 1.5, by 2011, however, this trend was almost entirely reversed, and the U.S. led world production [6]. This turn-around was a much-needed stimulation for the nation’s economy and job market.

![Figure 1.5 U.S. natural gas gross imports and exports, and net imports, from 1973-2011 [59].](image-url)
It is widely recognized that shale gas development within the U.S. creates domestic jobs and increases national revenue [6, 7]. Exploration and production processes directly and indirectly generate job demand in dozens of markets (e.g., services, labor, etc.) [19]. Nation-wide, hundreds of Americans have financially benefited from leasing their mineral rights to gas and oil companies looking to put well pads on their land [3]. Presently, the fertilizer, pharmaceutical, and plastics manufacturing companies are profiting by using inexpensive natural gas for energy, and natural gas powered fleet vehicles are gaining traction, nation-wide [3].

When it comes to studying the economic and social aspects of shale gas production via hydraulic fracturing, the Marcellus region seems to be the most investigated. A study by Considine, *et al.*, estimated that the activity of the natural gas industry within Pennsylvania added $11.16 billion in total revenue during 2010 [19]. Table 1.2 lists twenty business sectors which have directly and indirectly financially benefited from the natural gas industry in Pennsylvania. Often demand for commodities even outstripped the supply: As many Pennsylvanians can attest, finding a vacant hotel room in the western part of the state between 2007-2011 was almost impossible. In response to the sudden increase in demand brought on by natural gas operations, between 2006 and 2014, the hospitality industry in the Marcellus Shale region built over 60 new hotels in the region, raking in over $600 million in revenue and generating about 1,600 new jobs [29].

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6 At the time he wrote this document, Considine was a professor at Penn State University.
While the development of unconventional oil and gas resources has indelibly changed the fossil fuel outlook for the U.S., there are concerns that the country may not be able to economically develop its resources, and long-term costs of natural gas production could outstrip profits [7, 20]. Initially, natural gas production in the U.S. was high; however, in 2012 production rates outstripped demand and prices tumbled, dropping below $3/MMBTU\(^7\) ($3.17/GJ), as shown in Figure 1.6 [3, 30]. At the time of this writing, natural gas prices have continued to plunge and are now below $3/MMBTU – a far cry from early 2008 [30, 68]. And, as prices have declined, petroleum companies have curbed their production of natural gas, subsequently economically affecting dependent communities and industries [29, 31].

\(^7\) “MMBTU” is equivalent to “mmBTU,” and both mean “one million British Thermal Units (BTU).”
Figure 1.6 The fluctuating price of natural gas, as shown by Henry Hub Spot Prices. Adapted from data from [68].
1.6 Environmental Concerns

1.6.1 Hydraulic Fracturing Opposition

Across the U.S., hydraulic fracturing is a topic of heated environmental and economic debate [7]. According to the group “Americans Against Fracking,” in a collective bid to press for a nation-wide ban on hydraulic fracturing, nearly 30 national organizations and over 250 local organizations in 29 states have joined their coalition [32]. Most Americans, however, are either unaware of or undecided on the benefits and risks of the process [33]. In hotly contested areas of the country, however, this is not always the case. A 2014 survey found that 49% of Pennsylvanians closely follow the issue of hydraulic fracturing, with 54% supporting the process [34]. The question remains, though: In the face of the potential benefits previously discussed, why do so many people oppose hydraulic fracturing?

1.6.2 Aquifer contamination

The two most common concerns surrounding hydraulic fracturing is the possibility of natural gas or fracturing fluid escaping from wellbores into fresh groundwater aquifers [3, 35]. These seem to be legitimate and intuitive concerns since fracturing wells intersect these, and injecting fluid at high pressures into gas reservoirs could arguably displace gaseous hydrocarbons up through overlying strata and into groundwater aquifers. Another possibility is that the structural failure of a well casing or annulus during hydraulic fracturing allows thousands of gallons of pad to gush into a drinking water aquifer. Or perhaps an improperly sealed well annulus provides a pathway for natural gas to infiltrate overlying groundwater aquifers.

A popular and well-documented example of an alleged case of contamination from hydraulic fracturing is the saga of Dimock, Pennsylvania. Located about 20 miles North of
Scranton in rural Pennsylvania, most township residents obtain their household water from a shallow, groundwater well on their property. As part of the development of the Marcellus Shale gas play, Cabot Oil & Gas Corporation began drilling in Dimock. Following complaints from residents and the report of an explosion in an open well pit, the Pennsylvania Department of Environmental Protection (PADEP) began actively sampling residential drinking water wells in January 2009, as part of an investigation [36, 37].

In September 2009, Cabot was cited by the PADEP for two separate spills of hydrofracturing fluid, totaling nearly 8,000 gallons (30.3 m³), which polluted a creek and wetland [38, 39]. Because Cabot claimed that the fluid contained only 0.5% chemical lubricating gel, they argued that it was not hazardous, [39]. After the PADEP halted their operations for a few weeks, they were approved to resume drilling [38]. These incidents, however, clearly leveled Cabot directly in the sights of the PADEP, and in November 2009 the company was required to sign a consent order, promising to fix failing well casings in the Dimock area [36, 40].

In April 2010, the PADEP found Cabot to be noncompliant with the terms in the consent order, and the company was fined $240,000, their drilling activities were again suspended, and three of their wells – which were suspected to be leaking – were required to be capped [36, 40]. By the end of their investigation, the PADEP concluded that Cabot’s operations had contaminated 18 drinking water wells [41]. After a 2.5 year drilling ban, deliveries of freshwater to Dimock residents, and a $4.6 million settlement with the state (10.9% of which went to the state, and the rest to the affected households), the PADEP allowed Cabot to resume limited

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8 According to a PADEP regional director, the testing was focused on measuring “total dissolved solids, chlorides, specific conductivity, pH, alkalinity, hardness, sodium, calcium, barium, iron, manganese, potassium, and aluminum,” as all these could be possible indicators of well contamination from natural gas drilling operations [37].
operations [36, 41]. Residents, however, still carry forward with personal lawsuits against the company [41].

In Dimock, PA, and around the country, the battle over hydraulic fracturing viciously continues. Opponents of hydraulic fracturing have started a website titled “dimockproud.com” to promote their views and tell their stories, while Cabot’s External Affairs team also posted a blog, to soften their image and present their side of the story [42]. According to National Public Radio’s “StateImpact Pennsylvania” website, “[Dimock] has become ‘ground zero’ in the battle over whether or not hydraulic fracturing is safe” [43].

Naturally, Dimock is not the only case of claimed aquifer contamination from hydraulic fracturing. Generally, there are two common themes to claims of contamination in shallow, fresh groundwater aquifers from hydraulic fracturing: First, the presence of unique or common chemical elements – found in the hydraulic fracturing process, or in the deep, shale formations accessed by it; second, abnormally high concentrations of thermogenic methane\(^9\). In some so-called “proven instances” of drinking well contamination from oil and gas development, chemical additives distinct to hydraulic fracturing have been found in drinking water wells [3, 35, 44]. Also, studies have found thermogenic – not biogenic\(^{10}\) – concentrations in shallow groundwater aquifers, in the vicinity of shale gas wells [35]. Such findings fuel contamination claims attributed to hydraulic fracturing.

Despite the hype, studies have concluded that the chances of well casing failure are about one-in-five hundred billion [10]. Furthermore, wells in operation represent an area of low pressure. Thus, if nearby aquifers were impacted by these wells, the expected effect would be to

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\(^{9}\) Recall that natural gas is predominantly methane gas.

\(^{10}\) Biogenic methane refers to CH\(_4\) gas produced by shallow, subterranean microbial activity; whereas thermogenic methane is produced at great depths (>1,000 m; 3,280’) under high temperature and overburden pressure [65].
draw water from the aquifer into the producing well. Additionally, thousands of feet separate fractured formations from overlying, freshwater aquifers, decreasing the likelihood of contamination from hydraulic fracturing [3]. There are claims, however, that there may be natural fractures linking deep and shallow geologic formations, potentially enabling the subterranean migration of harmful elements [35].

Allegations of contamination regardless of the prestige of the claimant (e.g., state or federal regulatory agencies) must be tempered, however, by the knowledge that they are frequently either disproven or withdrawn entirely [45]. Additionally, analysis of groundwater aquifers which are located close to hydraulically-stimulated, natural gas wells often reveals no contamination [35]. Consequently, it is appears safe to conclude that the effects of hydraulic fracturing on underground freshwater aquifers (if any) are not well-understood, and, sadly, the debate will most likely rage for decades to come.

1.6.3 Greenhouse Gas Emissions and Carbon-foot print

Most of the concerns over greenhouse gas emissions produced by the hydraulic fracturing process focus on potential, undetectable well leaks, and, to a lesser extent, the equipment used [7, 12]. Because natural gas is predominantly methane – a colorless, odorless gas, considered to be one of the most damaging greenhouse gases – most environmentalists regard the potential for fugitive emissions from natural gas production wells with concern [3, 7, 46, 47]. In general, however, aside from these concerns, the greenhouse gas emissions which can be undeniably linked to hydraulic fracturing (i.e., those produced by the trucks and other heavy equipment used) are considered to be equal to or less than those generated by other petroleum production processes [47].
Likely the greatest greenhouse gas emissions involved in natural gas production do not come from accessing it, but rather its processing. Upon extraction, large volumes of raw natural gas are generally not immediately useful [2]. Furthermore, under ambient conditions, the gaseous nature of this fuel mixture has a very low density. Therefore, raw natural gas must either be compressed (creating compressed natural gas, CNG) or liquefied (hence, liquefied natural gas, LNG\textsuperscript{11}) to achieve effective transportation for future industrial or domestic use or storage [2].

![Figure 1.7 Comparison of carbon emissions per amount of energy consumed, for shale and conventional gas, coal, and diesel oil. Estimates are for a 100-year time horizon. Direct CO\textsubscript{2} (blue) refers to emissions of CO\textsubscript{2} during combustion; indirect CO\textsubscript{2} (orange) refers to emissions from processes necessary to develop and use the energy source; and methane (pink) represents fugitive emissions of methane, converted to equivalent value of CO\textsubscript{2} using global warming potentials [66, 67].](image)

\textsuperscript{11} As shown in Table 1.3, although LPG, LNG, and propane are misused as interchangeable terms, LPG is a more refined version of LNG – being mostly propane [2]. It is the end product of natural gas which most Americans encounter as 20 lb (9 kg) cylinders for outdoor grills, etc. Its physical properties are similar to LNG.
As shown in Table 1.3, however, compressing natural gas requires taking the mixture from ambient to very high pressures (>2,500 psi [17.3 MPa]), and turning it into a cryogenic liquid necessitates dropping its temperature to below 260°F (162°C) [3, 48, 49]. Depending upon the sophistication and size of the processing plant, producing compressed natural gas requires 2-5% the energy value of the processed gas and or liquefied petroleum gas demands 10-30% [49]. In addition to being energy demanding, these processing facilities are capital intensive [49].

Ironically, after refining and cryogenically condensing natural gas to liquefied natural gas, it is transported to its final destination where is allowed to warm, returning to the gas phase, for short-distance distribution through pipelines to consumers [3, 48]. Although little energy is required for this vaporization (see Table 1.3), overall this process represents a loss of energy. Thus, though the reasons are numerous and varying, questions regarding the overall economic soundness and environmental cleanliness of natural gas are being voiced in increasing numbers [50].

Table 1.3 Properties of compressed and liquefied natural gas [49].

<table>
<thead>
<tr>
<th>In-tank Properties</th>
<th>CNG</th>
<th>LNG¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical State</td>
<td>Gas</td>
<td>Liquid</td>
</tr>
<tr>
<td>Temperature</td>
<td>Ambient</td>
<td>-162°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>17.3-24.9 MPa</td>
<td>170-446 KPa</td>
</tr>
<tr>
<td>Density</td>
<td>0.13-0.19 kg/L</td>
<td>0.42 kg/L</td>
</tr>
<tr>
<td>SG</td>
<td>0.13-0.19</td>
<td>0.42</td>
</tr>
<tr>
<td>LHV²</td>
<td>46.892 MJ/kg</td>
<td>49.404 MJ/kg</td>
</tr>
<tr>
<td>Heat of Vaporization</td>
<td>n/a</td>
<td>0.51 MJ/kg</td>
</tr>
</tbody>
</table>

Values are for methane; natural gas is about 95% methane.
¹Physical properties of LPG are essentially the same.
²Source [60].

¹² Although CNG was historically used before LNG and less energy is required to create CNG, a higher density has made LNG the preferred form for long-distance transportation [2, 86]. Furthermore, the pressures of CNG make it unsuitable for pipeline distribution, and potentially more dangerous than LNG as a fuel source [2]. Consequently, LNG is the most common, refined product of natural gas today.
1.6.4 Noise & road traffic

Other common complaints about natural gas operations, particularly in the more heavily populated northeastern U.S., are increased noise levels and road traffic [3, 23, 51, 52]. Unconventional gas wells typically require a significantly larger surface footprint (3-6 acres) than conventional wells (1-3 acres) [3]. According to a 2010 estimate, 3,500 acres of land in Pennsylvania had been cleared for gas development – an area which was expected to increase to 82,000 acres within the next 20 years [23]. Naturally, this ever expanding drilling and production activity implies increasingly closer proximity to nearby residences and a higher volume of vehicular traffic, to support the site. Kolb aptly noted that although the negative aesthetic effects caused by hydraulic fracturing may not exceed other fossil-fuel production techniques, this close proximity to residential areas has perhaps drawn more public scrutiny and environmentalists’ ire toward hydraulic fracturing than is deserved [3].

1.6.5 Seismic Activity

Another key concern with hydraulic fracturing is the risk of inducing seismic activity (i.e., tremors or minor earthquakes) [3, 9]. Since the mid-20th century, scientists and geologists have known that the injection of fluid into underground formations can caused tremors, and recent research confirms that hydraulic fracturing activities are responsible for “very small magnitude earthquakes” in some locations [53, 54]. A 2009 to 2011 data review of injection-well locations in the Barnett Shale Play conducted by Frohlich found eight times more earthquakes than reported by the National Earthquake Information Center [55]. Most underground injection activity, however, is either aseismic (at least to a certain degree) or carries what is presently deemed a reasonable level of risk [56].
1.7 Summary

Hydraulic fracturing can be a controversial and polarizing topic. Consequently, it can be difficult to determine the truth of or real the significance of facts presented by both sides of the debate. As Sovacool wrote, “[B]ecause of [the] complicated and contested nature of [hydraulic fracturing]….the ‘debate’ may be irresolvable, since both ‘sides’ can point to an array of data supporting their claims, and simply ignore countervailing data that they do not like” [7]. In spite of this, a good summary of the widely-accepted pro’s and con’s of shale gas production (in the U.S.) is shown below, in Table 1.4.

Ultimately, the author has not encountered a single, reliable literary source which suggests a foreseeable cessation to hydraulic fracturing or shale gas production. In fact, even if the exploitation of unconventional natural gas resources in the U.S. ends, it will almost certainly continue in other regions of the world (e.g., Russia, China, India, etc.). Therefore, the correct question to ask does not concern the benefits or risks associated with the process, but, rather: How do we solve the undisputed present and anticipated environmental problems resulting from hydraulic fracturing?
Table 1.4 A brief summary table listing the pros and cons of shale gas production [7].

<table>
<thead>
<tr>
<th>Pro</th>
<th>Con</th>
</tr>
</thead>
<tbody>
<tr>
<td>5760 trillion cubic feet of recoverable gas potentially available and fortuitously situated close to major energy consumers such as China, India, and the United States and worth trillions of dollars</td>
<td>Extraction requires site specific, complex, capital intensive technology prone to leakage, accidents, and earthquakes, and may be dependent on carbon capture and storage to achieve long-lasting carbon gains</td>
</tr>
<tr>
<td>Affordable production prices 50–66 percent cheaper than ordinary gas that are then passed onto consumers and industries</td>
<td>Profit margins are unclear and may be negative due to the rapid depletion of wells and the inclusion of all social and environmental costs</td>
</tr>
<tr>
<td>The ability to “break” longstanding monopolies of natural gas supply (e.g. Russia or Venezuela)</td>
<td>Serious economic risks to conventional natural gas producers such as Qatar, Australia, Trinidad and Tobago, and Oman</td>
</tr>
<tr>
<td>Use in the electricity sector tends to lower overall greenhouse gas emissions intensity and lead to the retirement of coal-fired power plants</td>
<td>Under certain assumptions can have a higher footprint than coal and other fossil fuels and a more immediate impact on the climate due to the potency of methane</td>
</tr>
<tr>
<td>Can begin to substitute for petroleum and oil in the transportation sector, lowering the environmental impact of that sector</td>
<td>Has an equal propensity to “lock in” investments in fossil fueled infrastructure and displace energy efficiency, renewable electricity, and nuclear power</td>
</tr>
<tr>
<td>Creates thousands of jobs, millions of dollars of tax revenues, and billions of dollars of investment in each region that adopts widespread fracking</td>
<td>Is water intensive and therefore may not be possible in areas prone to water stress and can contribute to the serious deterioration of water quality and the release of radionuclides and local air pollution, threatening public health as well</td>
</tr>
<tr>
<td>Strongly endorsed by landowners standing to profit from shale gas leases, energy companies wishing to develop resources, and energy-independence-minded political leaders</td>
<td>Strongly opposed by community members without access to reserves, environmental groups and nongovernmental organizations, and renewable energy and nuclear power advocates</td>
</tr>
</tbody>
</table>
1.8 References


2.1 Using and Producing Water

2.1.1 The Real Concern: Lots of Contaminated Water

In order to work toward solutions to the environmental issues with hydraulic fracturing, it is important to understand what they are. Although many concerns exist over the risks hydraulic fracturing present to the environment and public health, as were presented in Chapter 1, many of these are unproven and may be unfounded. It is undeniable, however, that the handling and disposal of products and wastes – particularly fluids – from the fracturing process present a current risk to humans and the environment [1-3]. Unfortunately, spills can occur [4, 5].

Figure 2.1 The risks posed by hydraulic fracturing to water resources, divided by phases of natural gas production [7].
Furthermore, the chance of an accidental wastewater discharge increases with additional movement, handling or prolonged storage [6, 7]. Figure 2.1 provides a succinct and graphical summary of the risks posed to water resources by hydraulic fracturing operations, divided by the phases of water management before, during, and after well fracturing.

2.1.2 Where’s the water coming from & how much is there?

In order to understand the risks hydraulic fracturing fluids pose, their properties must be understood. Many misunderstandings and misconceptions surround these liquids, so it is important to distinguish between them. During the hydraulic fracturing process several common fluid types are used. Once the well has been stimulated using this technique, two distinct types of wastewater streams result. The amounts and compositions of process fluids can vary widely among companies, and wastewater chemistry and volume can vary across geography [4].

2.1.3 Down-well

The best way to categorize hydraulic fracturing fluids is by their use during the process. Before discussing the waste emanating from a well, the substances that are injected into the well should be discussed.

2.1.3.1 Drilling Fluids & Muds

When wells are drilled into the Earth, fluids and muds surround and accompany the drill bit. These fluids circulate cuttings, lubricate and cool the bit, stabilize the well bore, and control downbore fluid pressure [8, 9]. The oil and gas industry generally exercise great care when drilling through groundwater aquifers, because if any enters the well it is likely to form scale and
precipitant, clogging the well, its bottom casing perforations, or the hydrocarbon-rich formation [10].

Another name for drilling fluid is “slick water.” As its name implies, “slick water” is water used to reduce friction, during the drilling and pumping process. The most common friction reducer is potassium chloride but polymers, such as polyacrylamide, can also be used [8, 10, 11].

Another use for “slick water” is to decrease viscosity to aid in the creation of a complex fracture network in shale formations [10]. Complex fracture patterns in natural gas shale formations are required due to the stress-isotropic nature of shale. When fracturing in sedimentary rock, friction reducing additives should possess either an overall neutral or negative (anionic) charge, to prevent adsorption onto shale [11].

Drilling muds serve less intuitive purposes than do fluids. Drillers primarily use mud to stabilize the well, preventing blowouts when the bit cuts through high-pressure fluid reservoirs [8]. Drilling muds also serve to cool the bit and transport cuttings out of the well [12]. Bentonite clay is the most common and primary drilling mud constituent [8]. Bentonite is thixotropic (i.e., its viscosity decreases with increasing energy addition).

Generally, drilling mud and cuttings are considered their own waste streams, separate from fracturing brines [12]. Drilling mud is typically reused, while cuttings are landfilled [13, 14]. Consequently, these wastes will not be further discussed.
2.1.3.2 Fracturing Fluid

As its name implies, hydraulic fracturing is a water-intensive process [15]. Each well requires between three to five million gallons of water [8, 9, 16-19]. (The highest reported amount of water which the author has seen, is 13.2 million gallons [50,000 m$^3$], quoted by Kharaka, et al. [20]). The exact quantity required varies by well and geography [9, 20].

Fracturing fluid (also called “pad” or “stimulation fluid”) has two purposes [10]. The first purpose is to fracture the sedimentary rock and thereby liberate the natural gas trapped within. The second purpose of fracturing fluid is to transport proppant into these fissures, and create a stable, porous, high-conductivity zone through which gas can flow to the wellbore.

Viscosity is an important fracturing fluid property. Different liquid viscosities are desirable at different steps in the process [9, 10]. For example, a highly viscous fluid is better suited for creating primary fractures and transporting dense proppant. Low-viscosity fluid, however, is better at creating a deep network of secondary fractures, reaching deeper into the trapped hydrocarbon lens. These changes in liquid viscosity are achieved using man-made polymers [10]. Their exact composition and addition concentration, however, is usually only known to the well finishing company.

Once the well is fractured, a strongly acidic solution is pumped into the wellbore to clean it [8, 10]. These fluids are typically 15% HCl, although HF is sometimes added to clean out trapped or remaining drilling muds [8,10]. In addition to cleaning the wellbore, these acidic solutions can also increase formation porosity near the wellbore via “matrix acidizing” [10].
2.1.3.3 Proppant mobilizer

During fracturing, fluid bears the pressure formerly borne by the rock. Hydrocarbons must freely flow, however, through these fissures to the wellbore. Therefore, the fluid cannot remain, but due to depth, the overburden stresses persist. Consequently, proppant is used to bear this pressure, “propping” the cracks open [9]. Due to its favorable conductivity, transportability, and particle strength, sand is the most common proppant [10].

Because sand is denser than water, if added to pure water or a less viscous, less dense, water-based fracturing fluid, it would simply settle to the well bottom, rather than filling the fractures. Consequently, transporting proppant from the wellbore into the cracks requires specialized solutions [10]. Of these, foamed gels or gelled fluids are the most common [8]. Cross-linkers in these solutions raise the mobilizing liquid’s viscosity, effectively depositing the proppant within the rock fissures.

2.1.4 Up well: What comes back up

2.1.4.1 Flowback

Once a well has been fractured and the formation’s cracks filled with proppant, well pressure can be released. This pressure release allows fluid to return to the surface [21]. This water is aptly called “flowback.” Flowback quantity varies widely, from as low as 10% up to 70% of the injected liquid volume [4, 8, 9, 14, 16, 19, 20, 22]. This extreme variation is due to disparities in well geography, depth, length, etc. [4, 23].

A 2008 Marcellus Shale Gas Play assessment stated that the wastewater amount from the hydraulic fracturing process might be less than four million gallons per day (15,000 m³/d), but
that this number would increase as more wells were drilled [17]. In 2011, Pennsylvania wells produced over 330 million gallons (1.25 million m$^3$) of flowback [14]. It has been estimated that development of the entire Marcellus Shale Gas Play will result in 456 million barrels (19.2 billion gallons; 73 million m$^3$) of flowback [14].

### 2.1.4.2 Produced Water

Water-based fluid emanating from oil or gas wells is not an uncommon or recent phenomenon [8]. Traditionally, this wastewater is called “produced water,” and occurs throughout the well’s lifetime [10, 21]. Generally, well age distinguishes between flowback and produced water. While there is no formally established time period delineating the two wastewaters, fluid emanating from a hydraulically fractured well within a half to two months after well completion is considered flowback, and everything after that is produced water [14, 20, 22, 23].

Known by many names – “brine,” “formation,” or “connate water” – this fluid previously resided within the hydrocarbon-laden, geologic formations [2, 14, 24]. Although petroleum engineers would prefer not to extract formation water, removing hydrocarbon product changes formation pressure, causing the brine to simultaneously move to the low-pressure region around the well [2]. Using oil-water separation techniques, produced water is typically separated from petroleum product and stored in tank beside the well, which is routinely emptied by vacuum trucks, taking it for disposal [10, 25].

Generally, flowback comes from a hydraulically fractured more rapidly than does produced water. As the well ages, however, the ratio of produced water to hydrocarbon product increases [2]. In a report prepared by T. Hayes, of the Gas Technology Institute, it was reported
that between 60 and 90 days following a well’s completion, water-based liquid production was less than 2,310 gallons per day (8.7 m$^3$/d) [19]. Rahm, et al., casually remark that the rate of produced brines is typically 260-530 gallons per day (1-2 m$^3$/d) [12]. Kharaka, et al., cite a range around 530 to just over 2,100 gallons of produced water per day per well (2-8 m$^3$/d/well) [20].

According to Dores, et al., “[Produced water] is the highest volume liquid waste stream generated in the petroleum industry” [26]. Globally, hundreds of millions of gallons of produced water are generated daily [24, 27]. The complete development of the Marcellus Play alone is expected to yield 22 billion gallons (83 million m$^3$) of produced brine [14]. Due to the high volume, the collection, handling, storage, and treatment or disposal of produced water is a significant cost to the petroleum industry [2].

### 2.1.5 Concluding Remarks

Although when compared to many other human activities (e.g., industrial production processes, agriculture irrigation, etc.) hydraulic fracturing does not require a large water volume, there are still legitimate concerns [8, 9, 17]. First, water for hydraulic fracturing is typically locally procured; however, in many of these regions, fresh water is a scarce and precious commodity [9, 28]. Furthermore, hydraulically fractured natural gas wells produce large volumes of flowback and produced brine which consistently are contaminated by organic and inorganic compounds [23].
2.2 Contamination

It has been established that all oil and natural gas wells produce wastewater. Also, the fact that hydraulically fractured wells have chemical-containing solutions injected into them has been introduced. The specific compositions of these injected and produced liquids, however, have not yet been discussed. Understanding these fluids at a more detailed and comprehensive level will provide a more accurate picture of the risks posed by hydraulic fracturing’s wastewater products.

2.2.1 Down-well chemicals

Hydraulic fracturing fluid is a complex chemical mixture, specifically engineered to perform various functions either simultaneously or at differing time intervals during the fracturing process. The combination of minimal disclosure by companies engaged in hydraulic fracturing and a wide array of chemicals used, however, make it almost impossible to truly know fracturing fluid’s composition. For example, fourteen oil and gas companies reportedly used 780 million gallons (3 million m$^3$) of “hydrofracturing products” (i.e., chemical mixtures; not including water) during 2005-2009 [29]. Their report listed a staggering list of 750 “chemicals and other components” used in the process [29].

To further complicate the situation, most hydraulic fracturing fluid mixtures are considered proprietary, and the Energy Policy Act of 2005 (sometimes called the “Halliburton loophole) amended the Safe Water Drinking Act to exempt “fluids or propping agents (other than diesel fuels) pursuant to hydraulic fracturing” from federal disclosure requirements [9, 15]. States, however, are gradually increasing pressure on gas companies to reveal information on chemical constituents [9, 20]. Sometimes, though, fluid chemical composition is unknown to the
drilling company, as they are purchased from a third party who protects their intellectual property as “trade secret” [29]. This lack of transparency coupled with limited completed health and environmental impact studies has led some state and local governments to take unilateral action against hydraulic fracturing (e.g., NY state has banned hydraulic fracturing altogether) [5, 15, 30, 31].

Although it is difficult to predict the composition of “fracturing fluids,” some generalities can be made. It is generally accepted that fracturing fluid is 80-99% water by volume [32, 33]. The pH is circumneutral (6-8) [17]. While most additives are organic compounds, metals such as lead and copper are sometimes added [29]. Other inorganics (e.g., borate, titanate, zirconate, etc.) are commonly added as cross-linkers to increase apparent viscosity, since reservoir temperatures are quite warm (175-200°F; 79-93°C), reducing the viscosity increase from polymers [10]. Guar or hydroxypropyl guar are commonly added to fracturing fluid to increase viscosity; however, the concentration is usually very low – about 0.25-0.7% (by weight) [9, 10]. Guars are linear gels, produced from a plant seed, which makes them economic and biodegradable [1, 69]. They are commonly used as thickeners in foods [69].

The practice of adding organic chemicals to fracturing fluid is historic and extensive. The best example is the use of diesel fuel as a hydraulic fracturing fluid [8]. From 2005 to 2009, the most widely used organic chemical in hydraulic fracturing was methanol, with isopropyl alcohol and ethylene glycol coming in a close second and third [8, 29]. Methanol is used as an anti-freeze agent and lubricant [34]. Both methanol and ethylene glycol are hazardous air pollutants, and dissolved methanol is virtually untreatable by any membrane filtration system [8, 35]. Other key organics added include iron control polymers (the formation of siderite [FeCO₃] is considered particularly undesirable during the process) friction reducing polymers, and other
anti-scalants [11]. A common organic additive which is of concern is ethylene glycol monobutyl ether (2-butoxyethanol or “2-BE”), which is a common foaming agent or surfactant shown to be especially harmful to the human body [29]. Biocides are also commonly added to prevent plugging of wells or producing formations by bacteria [10].

While there are undoubtedly toxic chemicals added to fracturing fluids, what goes down the well may not be as important as what comes back up.

2.2.2 Up-well chemicals

More heavily documented and publicized than the chemical composition of down-well fluids are those of the flowback and produced wastewaters. Generally, chemistry and amount vary greatly across wells [2]. However, many of the key chemical constituents are the same. The best approach is to divide them into organic and inorganic categories and then consider the most common contaminants.

2.2.2.1 Organic

Produced waters contain dispersed oil and dissolved or soluble organic compounds [2]. Generally, wastewaters from natural gas processes contain higher concentrations of low molecular-weight aromatic hydrocarbons (e.g., BTEX) than those from oil production processes [2]. Jiang, et al., measured 720 mg/L of total organic carbon (TOC) in “flowback” (possibly produced) water, from a gas well in the Marcellus play [16]. In their extensive review of flowback water data from PA, NY and West Virginia. wells, Abualfaraj, et al., reported concentrations of Dibromochloromethane, Vinyl chloride, Benzo(a)pyrene, Pentachlorophenol,

---

13 Because this paper’s focus is separating dissolved (and suspended) solids from water-based oil and gas wastewater, discussion of organics commonly found in flowback and produced brines will be brief.
Benzene, 1,2 Dichloroethane, 1,1,2 Trichloroethane, 1,2 Dichloropropane, Carbon tetrachloride, Hexachlorobenzene, Heptachlorexpoxide, Dinoseb, and Heptachlor above their federal maximum contamination levels (MCLs) [33].

2.2.2.2 Inorganic

2.2.2.2.1 Total Dissolved Solids

Hydraulic fracturing wastewater has extremely high salinity concentrations [14]. This hyper salinity, typically represented in total dissolved solids (TDS) concentration, is the primary contaminant of concern in oil and gas wastewaters [2, 36]. Since the fracturing fluid itself is not hypersaline, these dissolved salts’ exact origin is unknown [37]. There are two hypotheses regarding how flowback and production fluids have come to be so saline: acidic sedimentary

Table 2.1 Commonly encountered concentrations for major, reoccurring constituents of flowback and produced brine wastewaters emanating from natural gas wells in the Marcellus Shale gas play [4, 32]. The “single well” columns are for the same well. “Early” and “late” refer to time after well completion.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Single well (early) (mg/L)</th>
<th>Single well (late) (mg/L)</th>
<th>Multiple wells (late) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dissolved solids</td>
<td>66,000</td>
<td>150,000</td>
<td>261,000</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>27</td>
<td>380</td>
<td>3200</td>
</tr>
<tr>
<td>Hardness (as CaCO₃)</td>
<td>9100</td>
<td>29,000</td>
<td>55,000</td>
</tr>
<tr>
<td>Alkalinity (as CaCO₃)</td>
<td>200</td>
<td>200</td>
<td>1100</td>
</tr>
<tr>
<td>Chloride</td>
<td>32,000</td>
<td>76,000</td>
<td>148,000</td>
</tr>
<tr>
<td>Sulfate</td>
<td>5</td>
<td>7</td>
<td>500</td>
</tr>
<tr>
<td>Sodium</td>
<td>18,000</td>
<td>33,000</td>
<td>44,000</td>
</tr>
<tr>
<td>Calcium, total</td>
<td>3000</td>
<td>9800</td>
<td>31,000</td>
</tr>
<tr>
<td>Strontium, total</td>
<td>1400</td>
<td>2100</td>
<td>6800</td>
</tr>
<tr>
<td>Barium, total</td>
<td>2300</td>
<td>3300</td>
<td>4700</td>
</tr>
<tr>
<td>Bromide</td>
<td>720</td>
<td>1200</td>
<td>1600</td>
</tr>
<tr>
<td>Iron, total</td>
<td>25</td>
<td>48</td>
<td>55</td>
</tr>
<tr>
<td>Manganese, total</td>
<td>3</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>10</td>
<td>18</td>
<td>260</td>
</tr>
</tbody>
</table>
rock dissolution, and 

*in situ* brines [38]. It seems generally accepted that acidic dissolution is not responsible since the pH of flowback and produced water is generally circumneutral, and therefore acidic sedimentary rock dissolution would seem an unlikely source [2, 22]. Conversely, the existence of hypersaline, *in situ* brines is fact [24, 39].

Natural gas wastewaters’ salinity ranges widely. Typically their TDS concentration closely mirrors that of produced brines (*i.e.*, > 100,000 mg/L) [18, 21, 40]. In general, 200,000-300,000 mg/L salinities for both produced brines and sometimes flowback are commonly reported [12, 14, 16, 22, 33]. However, the TDS concentration of flowback emanating from a well just after fracturing can be below 1,000 mg/L [16, 19].

As water returns to the surface, following hydraulic fracturing, salinity concentration increases [19, 40]. Figure 2.2 gives a representative example of this phenomenon for a hydraulically fractured well in the Marcellus Shale Gas play. Pennsylvania regulators are
concerned about future wastewater streams from existing wells, which they believe could exceed 300,000 mg/L (TDS) for 20 to 30 years per well [41].

In elevated concentrations, salt can be toxic [6]. To put these wastewater salinities in perspective, according to the U.S. Environmental Protection Agency (USEPA) and World Health Organization (WHO), the upper TDS limit for potable water is 500 mg/L [36]. For the U.S., this TDS concentration is the national Secondary Drinking Water Regulation level [42].\(^\text{14}\) Similarly, the 500 mg/L value given by the World Health Organization is not a regulation, but merely the definition of a “high” TDS level [87].\(^\text{15}\) By comparison, the TDS concentration of open-ocean seawater is 35,500 mg/L, of which most is sodium chloride. In 2010, Pennsylvania specifically targeted the oil and gas industry by requiring the discharge of waste water from natural gas production not contain more than 500 mg/L TDS (as a monthly average) [41].

The terms “TDS” and “salts” are generic, and can be subdivided into cations and anions. Primary cations in natural gas wastewater are sodium, potassium, iron, calcium, magnesium [17]. Major anions in natural gas wastewater are chloride, sulfate, carbonate, and bicarbonate [17]. These all occur at elevated concentrations [16, 19, 41, 42]. Aluminum, antimony, arsenic, barium, beryllium, cadmium, copper, lead, nitrite (as N), selenium, and thallium have also been found in flowback at concentrations above their respective federal maximum contamination levels [33].

A polyatomic anion listed above which deserves special mention is sulfate ($\text{SO}_4^{2-}$). In their wastewater data review, Haluszczak, et al., noted that sulfate concentrations – which were

\(^{14}\) According to the USEPA, Secondary Drinking Water Regulations are “Non-enforceable Federal guidelines regarding cosmetic effects (such as tooth or skin discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water” [42].

\(^{15}\) According to the WHO, drinking water with TDS $\leq$ 300 mg/L has an “excellent” taste. Water with a TDS concentration between 300-600 mg/L is “good,” and 600-900 mg/L is “fair” [87].
already low, at less than 500 mg/L – decreased over time, in flowback and/or produced waters. Such a finding is also confirmed by Hayes, who found 2.4-106 mg/L sulfate in 19 wells, five days after completion, versus <10-89.3 mg/L for all but two of the same 19 wells, 14 days after completion [19]. Haluszczak, et al., speculate was that this is caused by a naturally low concentration of $\text{SO}_4^{2-}$ in in situ brines [22]. Jiang, et al., reported a mere 12.9 mg/L of sulfate in “flowback” (or possibly produced) water from a gas well drilled in the Marcellus play [16].

With a relatively high Secondary Drinking Water Regulation concentration of 250 mg/L, sulfate in hydraulic fracturing wastewater is not monitored as a potential health or environmental risk, but because of its potential for process interference [42]. Oil and gas wastewater typically contains high concentrations of barium [46]. Barium and sulfate readily and rapidly form an insoluble scale (barite; $\text{BaSO}_4$) [47]. Not only is this scale nearly impossible to remove, but radium co-precipitates with barite, making the scale radioactive [47].

2.2.2.2 Naturally Occurring Radioactive Material (NORM)

A serious issue of concern regarding flowback and produced water from shale gas wells is radionuclides, typically referred to as naturally-occurring radioactive material or technologically-enhanced naturally-occurring radioactive material (TENORM) [15, 48]. The two radioactive elements of greatest concern are uranium and radium. Although it is uncommon to find significant uranium concentrations in produced or flowback water, Haluszczak, et al., detected 93 mg/L of uranium in a natural gas production well in Fayette County, PA in August 2009 [22]. Data reviewed by Abualfaraj, et al., showed median concentrations of 0.44 pCi/L of U$^{234}$, 0.14 pCi/L for U$^{235}$, and 0.33 pCi/L for U$^{238}$ [33]. The maximum contaminant level for
uranium is 0.03 mg/L (which is about 10 pCi/L for \( \text{U}^{238} \) – the most common, natural uranium isotope) [42].

An alkaline earth metal, radium has two isotopes of particular concern: \( \text{Ra}^{226} \) and \( \text{Ra}^{228} \). Radium-228 is a daughter product of Thorium-232, while Radium-226 is a daughter product in Uranium-238’s decay series. Haluszczak, et al., found \( \text{Ra}^{226} \) concentrations ranging from zero to over 5,500 pCi/L, and \( \text{Ra}^{228} \) concentrations from zero to over 700 pCi/L [22]. The maximum contaminant level for combined \( \text{Ra}^{226} \) Radium and \( \text{Ra}^{228} \) Radium is 5 pCi/L [42]. Abualfaraj, et al., reviewed data from four sources for flowback water from PA wells, showing median activities of gross alpha activity of 13,000 pCi/L, \( \text{Ra}^{226} \) of 1,300 pCi/L, and \( \text{Ra}^{228} \) 230 pCi/L [33].

Another alkaline earth metal commonly found in flowback and produced brines is barium. For drinking water, the U.S. federal maximum contaminant level for barium is 2 mg/L [42]. Pennsylvania mandates natural gas production wastewater discharges to contain less than 10 mg/L barium as a monthly average [41]. Haluszczak, et al., found barium concentrations ranging from just under 5 mg/L to over 6,000 mg/L [22]. Hayes found 21.4-13,900 mg/L of barium in flowback water samples from 19 wells, five days after well completion [19]. Jiang, et al., reported 697 mg/L of barium in “flowback” (or possibly produced) water from a gas well drilled in the Marcellus play [16]. Data reviewed by Abualfaraj, et al., had a median concentration of 164 mg/L, with a maximum of 13,900 mg/L for 220 samples [33].

2.3 Past Wastewater Disposal Options

Historically, oil and gas industry wastewater has had an almost sadly comical fate. Prior to the 1970’s, produced water was dumped in surface water bodies, devastating the receiving waterways [20]. In some cases, wastewater was kept indefinitely in a lined settling pond, near
the well, relying on evaporation to reduce the volume [13]. Less common but highly publicized hydraulic fracturing wastewater fates were landfilling and road spreading (to melt ice and snow, or reduce dust on unpaved, gravel roads) [12].

At the outset of the hydraulic fracturing boom, process wastewater was sent to local waste water treatment plants (WWTPs) and publically owned treatment works (POTWs) to circumvent industrial waste discharge regulations [9, 12, 15, 49]. Studies suggested, however, that these facilities could not adequately treat natural gas wastewater and so such discharges were very short-lived [49].

Fortunately, increased regulation and oversight have almost entirely stopped natural gas wastewater from going to waste water treatment plants or publically owned treatment works [12]. A regulatory practice, in Pennsylvania, responsible for this is the DEP’s required Water Management Plan for each drilling permit [12, 17]. Therefore, before a well can be drilled, the owner must submit a waste disposal plan. But what are petroleum and natural gas companies to do with their wastewater?

2.4 Current Wastewater Fate

2.4.1 Deep Well Injection

One legal and common oil and gas wastewater disposal method is underground well injection [2, 9, 28, 50]. Regulated by the Federal Safe Water Drinking Act’s Underground Injection Control Program (UIC), there are Class I and II disposal wells nation-wide [2, 17]. Oil and gas wastewater is predominantly disposed of in Class II-D wells [9, 51]. Due to its very low cost, this is the industry’s preferred disposal method [1, 28]. These wells’ capacities, however, are limited [17].
Recently, as the price of natural gas has dropped, drilling has slowed. This has increased the proportion of produced brine to flowback, thereby increasing injection disposal amounts (versus reuse; see the following section) [12]. In PA during 2011, the injection wells’ reported use for produced brine disposal increased almost 130% [14]. In PA, however, there are only eight permitted disposal wells [17]. Thus, wastewater is trucked to disposal wells in nearby states – particularly, West Virginia, Ohio, and Maryland [12, 14]. Transporting this wastewater, however, can be expensive.

2.4.2 Reuse

As surface water discharge regulations tighten, transportation costs fluctuate, and down-well disposal capacity shrinks, hydraulic fracturing flowback reuse is growing in popularity [9, 11, 12, 25]. This is particularly true in the Marcellus region, because of the few available injection disposal wells [9, 25]. In 2013, Barbot, et al., reported that most Marcellus Shale flowback water in PA

<table>
<thead>
<tr>
<th>Disposal state</th>
<th>Produced water (bbl)</th>
<th>Flowback (bbl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD Brine or industrial waste treatment plant</td>
<td>114</td>
<td>0</td>
</tr>
<tr>
<td>NJ Landfill</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NY Landfill</td>
<td>445</td>
<td>1,320</td>
</tr>
<tr>
<td>OH Brine or industrial waste treatment plant</td>
<td>171,077</td>
<td>97,898</td>
</tr>
<tr>
<td>OH Injection disposal well</td>
<td>2,348,702</td>
<td>140,063</td>
</tr>
<tr>
<td>OH Landfill</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OH Other</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PA Brine or industrial waste treatment plant</td>
<td>1,052,182</td>
<td>531,970</td>
</tr>
<tr>
<td>PA Landfill</td>
<td>95</td>
<td>1,197</td>
</tr>
<tr>
<td>PA Injection disposal well</td>
<td>5,346</td>
<td>110</td>
</tr>
<tr>
<td>PA Municipal sewage treatment plant</td>
<td>26,379</td>
<td>6,784</td>
</tr>
<tr>
<td>PA Unknown</td>
<td>331,182</td>
<td>14,320</td>
</tr>
<tr>
<td>PA Reuse other than road spreading</td>
<td>2,216,889</td>
<td>3,774,078</td>
</tr>
<tr>
<td>PA Reuse other than road spreading</td>
<td>2,833,297</td>
<td>3,301,804</td>
</tr>
<tr>
<td>PA Other</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>WV Brine or industrial waste treatment plant</td>
<td>23,484</td>
<td>0</td>
</tr>
<tr>
<td>WV Injection disposal well</td>
<td>10,305</td>
<td>3,964</td>
</tr>
<tr>
<td>WV Landfill</td>
<td>0</td>
<td>520</td>
</tr>
<tr>
<td>Unk Injection disposal well</td>
<td>45,973</td>
<td>4,559</td>
</tr>
<tr>
<td>Unk Landfill</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total intrastate transfer</td>
<td>6,465,370</td>
<td>7,650,263</td>
</tr>
<tr>
<td>Total interstate transfer</td>
<td>2,554,127</td>
<td>243,765</td>
</tr>
<tr>
<td>Unknown state</td>
<td>45,973</td>
<td>4,559</td>
</tr>
<tr>
<td>Total</td>
<td>9,065,470</td>
<td>7,878,587</td>
</tr>
</tbody>
</table>

"Unknown" indicates a treatment/disposal location was not indicated in the waste product report. "PA" indicates waste reports had no state disposal location, but it was assumed to reused in Pennsylvania for analyses. "Unk," no identifying record for state; bbl, barrels.
was stored in lagoons or tanks, awaiting future reuse [21].

As far back as the mid 1990’s, reuse of oil and gas wastewater was on the rise [2]. In 2009, the well-known gas company Range Resources became a reuse pioneer, using 160 million gallons (600,000 m³) – 28% of which was recycled – to successfully, hydraulically fracture 44 wells [25]. With a successful history, flowback reuse as fracturing fluid has steadily gained in popularity, to the point where it is now common practice [52].

Although flowback reuse is possible, it is complicated and can be expensive. Generally, cost and difficulty increase with rising salinity [1, 20]. Some research has shown (see Figure 2.3) that brine salinity increases with reuse. Also, with minimal to no treatment between recovery and reuse, the potential for formation damage from inorganic precipitates (particularly
CaCO₃) is a major concern for drilling companies [10]. Some innovative companies, however, use selective and good house-keeping processes to isolate and store the initial flowback, which tends to be less “contaminated” [17].

As with deep-well injection, reuse can have high transportation costs. Although Rahm, et al., reported that in 2011 the average distance traveled by hydraulic fracturing wastewater (~ 60 miles) decreased 30%, in general wastewater cannot always be stored onsite, awaiting future reuse [12]. Many oil and gas companies lack their own fluid storage facilities. Therefore it must be transported to a holding facility, to be moved again to a new well site at a later date. These costs are a major industry concern [17]. Furthermore, reuse only continues as long as new wells are drilled. Consequently, reuse is an option, but not a long term-solution for both flowback and produced brines.

2.5 Conventional Wastewater Treatment Options

Presently, the oil and gas industry relies heavily on reuse and re-injection as wastewater disposal options. As discussed, however, both these options are questionable. If the oil and gas industry was required to remediate this wastewater, what technologies are available to them?

2.5.1 Reverse-Osmosis

A leading desalination method is reverse osmosis. Traditionally, reverse osmosis techniques are broken down into two categories: brackish water reverse osmosis systems, designed for source waters with salinities from 500 to 15,000 mg/L, and seawater reverse osmosis elements, suitable for source fluids with salinities from 15,000 mg/L to 45,000 mg/L [36]. The TDS range for seawater is 15,000 to 36,000 mg/L, with an average salinity of 34,000 mg/L [36, 43]. Typically about 30,000 mg/L is sodium chloride [45]. About 60% of the world’s
desalination plants use reverse osmosis technology, 34% use thermal distillation, and the remaining use electrodialysis and ion exchange technologies [36]. Two key benefits of reverse osmosis are lower energy and lifecycle costs than thermal distillation [53]. Capital costs are cited as being between 80 cents to $7 per gallon per day [53]. Average seawater reverse osmosis energy use is 3.1 kWh per cubic meter of fresh water produced (0.011 MJ/kg, assuming $\rho_w = 1,000 \text{ kg/m}^3$), where only 40 to 55% of the source is converted to freshwater [36].

There are several case-studies that investigated the potential of reverse osmosis for treating oil and gas wastewater. Brandt, et al., used a pilot-scale reverse osmosis unit to successfully concentrate a 183.5 gpm (11.6 lps) flow with a 7,000 ppm TDS concentration [50]. A chemical pre-treatment step preceded this, however, precipitating out calcium carbonate (CaCO$_3$), barium sulfate (BaSO$_4$), calcium sulfate (CaSO$_4$ $\cdot$ H$_2$O), strontium sulfate (SrSO$_4$), and calcium fluoride (CaF$_2$) and adding HCl to buffer the pH to just below neutral.

Jiang, et al., investigated the treatment of “flowback” (though, this most likely includes produced water; the authors were not clear regarding when the fluid was collected from the well) from a hydraulically fractured, natural gas well in the Marcellus play, using ceramic membranes and ion-exchange resins [16]. Based on their own findings, the authors state that the high TDS levels necessitate high-powered, energy-intensive pumps for reverse osmosis, and the high total organic carbon levels they found can cause serious membrane fouling. Further, this study found that microfiltration ceramic membranes (0.8 and 0.2 μm) were effective at removing total suspended solids from flowback water, but were relatively ineffective at removing TDS and total organic carbon. Also, the 0.2 μm microfilter clogged within 30 minutes; whereas, a 1.4 μm filter did not clog but was not effective. The authors attempted various filters-in-series configurations, but the results were not outstanding when considering total organic carbon removal and
conductivity reduction (the authors correlated conductivity directly to TDS). Ultimately, Jiang, *et al.*, suggested that, due to the complex and highly concentrated chemistry of the flowback, no single remediation technique can be an on-site, cost-effective solution.

Fouling is a common problem in reverse osmosis. The problem is particularly acute in treating oil and gas wastewater, because even 0.02 mg/L or more of organic colloids can accelerate reverse osmosis membrane fouling [36]. In attempting to treat Marcellus flowback He, *et al.*, found pore blockage due to submicron particles to be the primary cause of membrane fouling, using 0.22 μm membranes [40]. Their two flowback water samples had TDS concentrations of 38,000 and 166,484 mg/L.

Typically, when the TDS concentration of flowback does not exceed 20,000 mg/L, reverse osmosis is the preferred method treatment method [13]. In a water treatment technology fact sheet, ALL Consulting, LLC, advises potential clients that although the natural gas industry uses reverse osmosis to remediate their wastewater, the upper TDS limit for even the most avant-garde reverse osmosis system is 45,000 mg/L [53]. Gaudlip, *et al.*, gives a similar upper TDS limit of 40,000 mg/L, for effective reverse osmosis treatment [17]. The highest TDS concentration provided for reverse osmosis, found by the author, is given by Arnal, *et al.*, at 70,000 mg/L, who call it the “technical limit of [reverse osmosis]” [54].

There’s another potential problem: reverse osmosis systems designed to treat hydraulic fracturing wastewater face severe operational problems due to the brine’s complex chemistry and high organic content [17]. To avoid corrosion and handle the high pressures required, reverse osmosis systems must be constructed using noble metals (e.g., titanium) [36]. To prevent membrane damage, most reverse osmosis systems also require chemical pre-treatment to remove...
suspended solids, oxidized metals, and scaling minerals, prior to the wastewater entering the system [36, 50].

Another potential downside to reverse osmosis is the high pressure required. More than half of a seawater reverse osmosis desalination plant’s energy goes to salt-water separation [36]. Some reverse osmosis systems can even require as much as 600-900 psig [17]. As the TDS concentration increases by 100 mg/L, osmotic pressure also increases by 0.07 bar (1 psi; 7 kPa) [36]. For example, a brine with 35,000 mg/L TDS has an osmotic pressure of approximately 24.5 bar (355.34 psi; 2.45 MPa), which must be overcome [36].

Reverse osmosis systems exist in many configurations, with varying types of membranes, specialized energy or pressure recovery devices, and so on. Their effectiveness at treating a solution with a TDS concentration exceeding 70,000 mg/L, however, is questionable. Considering the elevated TDS concentrations and complex chemistry of flowback and produced brines, reverse osmosis is not a particularly appealing remediation technique.

2.5.2 Ion exchange

If reverse osmosis most likely cannot treat oil and gas wastewater, then it should come as no surprise that ion exchange is scarcely effective. At its core, ion exchange uses an ion-loaded resin to replace dissolved ions in water. The technology is commonly used in domestic and industrial water softening, and the resin can be recharged once the replacement ions are exhausted. It’s applicable over a very limited TDS concentration range, about 100 to 7,000 mg/L [27, 36, 55]. Resin life, however, can be almost a decade, and energy costs are very low – about 0.07 kWh/bbl (0.0016 MJ/kg) [27]. Chemical pre-treatment, however, is a definite requirement [16, 27, 55].
In their study, Jiang, et al., found that although microfiltration did not greatly improve the quality of flowback water, subsequently passing it through an ionic resin chamber, at 20 mL/min (0.005 gpm), resulted in a dramatic reduction of the concentration of key anions and cations [16]. They also found that about 90% of the total organic carbon concentration (from 720 to 82 mg/L) was reduced, following ion exchange.

It is important, however, to note the following. First, Jiang, et al., used “flowback” water with a TDS concentration under 45,000 mg/L. Although this is about six times more than other sources state ion exchange to be capable of treating, this TDS concentration is significantly lower than most reported concentrations. Second, although the overall system (membrane microfiltration followed by ionic exchange) is well within the hydraulic fracturing wastewater treatment cost estimate ($0.12-0.25 per gallon) provided in 2010 by the PA Environmental Quality Board, it is still three times the cost of reverse osmosis [56].

2.5.3 Evaporation

Conventional evaporation is the most traditional brine remediation technique. Conventional evaporation uses thermal energy to distill water – moving solvent H₂O molecules from the liquid to gaseous phase, leaving behind a more concentrated solution. In a 2009 article by Blauch, et al., [11] evaporation was touted as the only viable hydraulic fracturing wastewater treatment. This sentiment seems widely accepted [36].

There exist a myriad of techniques for thermal evaporation. Some common terms are multi-effect distillation, thermal compression, vapor compression, multiple effect evaporation, humidification-dehumidification, and single effect evaporation [43]. The effectiveness of
distillation-based desalination systems is commonly expressed as the clean water produced to
steam mass flow rate ratio – called the gain output ratio [57].

2.5.3.1 Multi-stage Flash evaporation

Multi-stage flash evaporation is the oldest thermal evaporative process and one of the
first commercially-available thermal desalination technologies [36, 58]. By exposing preheated
water to vacuum pressures, a fraction of the warm water instantaneously flashes into steam [28].
This flashing phenomena occurs because the liquid – although only warm under ambient
pressure – is superheated when exposed to a sudden pressure drop, and the liquid’s surplus heat
instantly becomes latent heat of vaporization [58]. Flashing is important because it vaporizes
water significantly faster than conventional evaporation [58].

As its name implies multi-stage flash relies on “stages” or “effects” to improve overall
thermal efficiency [28]. This is required because the energy consumption of each stage exceeds
the theoretical minimum (i.e., the laws of thermodynamics still apply) [45]. In each effect, the
steam condenses on tubes, through which the source water flows (thereby preheating it), and is
collected on distillate trays as clean product [36]. For a very aggressive system, an entrainment
separator is used to separate high-salinity mist and low-salinity steam [36]. With each stage
producing only approximately one percent of the total plant distillate volume, a typical multi-
stage flash unit has 19 to 28 effects, though newest ones have 45-stages allowing them to
energetically compete with reverse osmosis in regions where energy prices are low [36, 57].

2.5.3.2 Mechanical Vapor Compression

Presently, the most common thermal distillation systems can be described as mechanical
vapor compression or recompression systems. These systems are thermally efficient [59].
However, they are technically complex, require large volumes, and are capital expensive. Like other thermal desalination techniques, vapor compression systems employ multiple effects to improve overall system performance, but mechanical steam compression pumps are added to the process, along with and extra heat exchangers.

Understanding vapor compression systems begins with the process’s second step: a single-effect generates steam [59]. This steam is mechanically compressed, increasing its temperature and saturation pressure [60]. This raises the condensation temperature of the steam, improving heat transfer efficiency, while inducing a slight negative (i.e., below atmospheric) pressure in the preceding effect [60, 61]. This lower pressure decreases the boiling point in the preceding stage [57]. The pumps force the steam into tubes located in the subsequent effect. As the steam condenses, the latent heat of condensation transfers across tubing walls contacting the liquid feed in the subsequent effect, becoming latent heat of vaporization.

Frequently in these vapor compression systems, liquid is sprayed onto the tubes in which steam condenses. This is known as a falling film evaporator, and is how early mechanical vapor compression systems functioned [60]. Vertical tube, falling film, vapor compression evaporators are gaining in popularity for treating oil and gas produced brines [26]. Although these systems

Figure 2.4 A conventional, multi effect distillation, sea water desalination unit [57].
are claimed to have better heat transfer properties, it is more likely that they are preferred due to their lower chances of fouling during operation [62]

2.5.3.3 Dewvaporation

Developed by engineers at Arizona State University, dewvaporation is a counter-current, convection and conduction heat exchange process, successfully applied to brines roughly two times more concentrated than seawater [27, 63, 64]. Based on the humidification dehumidification approach, because of their low-temperature and low-pressure nature, dewvaporation units can be constructed from plastic [64-66]. Low pressure is its primary selling-point [65]. As shown in Figure 2.5, influent brine is sprayed into one tower against an upflowing, hot air stream. Air can be heated by fuel combustion, solar power, or low-grade waste heat, from another process [66]. As the brine’s water evaporates, it is carried up and back into a co-joined tower chamber, where it cools and condenses on the tower walls, eventually running down for collection as clean effluent. The heat of condensation is transferred from the cooler to warmer tower, where it helps evaporate influent brine [46]. This process, however, may be more favorable in hot and arid states like Arizona than in humid and cold states like Pennsylvania.

A problem with this (and similar convective evaporation systems) is non-condensable gas [67]. In addition to flow turbulence and geometry, the presence of non-condensable gas is one of the most important factors affecting condensation heat transfer [68]. In traditional, closed...
thermal evaporators, non-condensable gases (e.g., CO₂, N₂, etc.) enter the system through leaks and/or as dissolved gases [68]. By preferentially concentrating at the liquid–gas interface, and thereby increasing mass transfer resistance, these non-condensable gases dramatically reduce condenser (and therefore, system) performance [67].

In a dewvaporation system, deliberately employing convective (i.e., hot gas) heat transfer, overall system thermal performance will be significantly less than competing thermal technologies. For example, the thermal conductivity of air is so low, a 1/1000th inch thick (0.0254 mm) air film has a thermal energy conductivity resistance equivalent to 3” (7.62 cm) of solid iron [69].

2.5.3.4 Thermal Evaporation Case Studies

Developed for use in maritime vessels, single effect evaporation is the simplest industrial form of conventional evaporation [43]. Although its thermal performance ratio is low, it is the building block of most other thermal desalination techniques [43]. Using a single effect evaporation type of unit, Brandt, et al., successfully concentrated 45.9 gpm (2.9 lps) reverse osmosis retentate brine using a pilot-scale, submerged heater [50]. (Recall: the reverse osmosis unit concentrated coal bed methane brine.) The TDS concentration of the brine was quite low – only 26,800 ppm. The authors found that the energy required per pound of water evaporated was in the range of 1,140 - 1,182 BTU’s (2.65 – 2.75 MJ/kg).16 This is close to water’s latent heat of vaporization (which is the minimum, theoretical energy requirement for water evaporation).

Koren and Nadav discuss two falling-film, mechanical vapor compression units used to treat produced water [70]. Their systems sprayed atomized feed onto the primary heat exchanger

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16 Where 1 BTU = 0.000293 kWh = 1.0548 kJ.
tubes. They processed 600 m$^3$/d (110 gpm; 83 m$^3$/h or 15 gpm each), with an average 56,000 mg/L salinity. For each unit, the distillate product flow was about 27 m$^3$/hr, and the total power usage was approximately 368 kW (including all the power for the pumps). They reported no scaling at 3,500 hours on one of their units. The specific energy consumption for each unit was reported as 13.6 kWh/m$^3$ (approximately 0.05 MJ/kg).

There are several commercial entities with proprietary, thermal distillation technologies for remediating oil and gas industry wastewater. One of these is a mechanical vapor recompression system called the NOMAD 2000, which is produced by Aqua-Pure Ventures, Inc. [66].

In summer 2011, the Research Partnership to Secure Energy for America (RPSEA), a 501(c)(3) nonprofit, conducted an evaluation of the NOMAD 2000 [61, 71]. At a north Texas facility, influent natural gas wastewater was preconditioned to remove suspended solids, petroleum hydrocarbons, iron and calcium. This chemical pretreatment step reduced the average influent TDS concentration from almost 60,000 mg/L to 45,000 mg/L. Treated brine was then sent three NOMAD 2000 units, each of which can accommodate up to 2,800 bbl/d.

Each NOMAD 2000 has three, skid-mounted modules – pretreatment, engine, and evaporator/heat exchanger [61, 66]. Using mechanical vapor recompression technology, the influent is separated into two streams – a distillate, at about 1,900 mg/L, and a 168,000 mg/L concentrate. The NOMAD’s engine is natural gas-powered, producing 700 HP (522 kW), at an assumed 35% efficiency [61]. The final result is 6.4 kWh/bbl distillate (0.15 MJ/kg distillate)$^{17}$.

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$^{17}$ One barrel is 42 gallons. 1.0 kWh = 3.6 MJ. Use a density of 8.34 lb/gal (3.78 kg/gal).
Eureka Resources, LLC, operates a commercial wastewater treatment facility in Williamsport, Pennsylvania using NOMAD units [25, 72]. At this location, Eureka offers wastewater pretreatment (primarily solids settling), dewasting (mostly methanol removal), crystallization (using a Salt & Evaporation Plants, Ltd., mechanical vapor recompression system), and distillation [73]. As their distillation technology, they claim that their facility’s NOMAD units can accommodate 10,000 barrels per day (1,580 m³/d) of wastewater influent with TDS concentration exceeding 100,000 mg/L, recovering between 50 to 95% the volume as distillate [74].

A commercial dewvaporation process technology currently treating hydraulic fracturing wastewater is AltelaRain® [27]. Unlike some other technologies, the AltelaRain® technology is well-reviewed [51, 66]. Although now a bit dated, a 2010 government-industry collaborative report published in 2011 provided a thorough review of Altela ARS-4000 pilot-scale systems operating in New Mexico and Pennsylvania. According to this report, the AltelaRain® process generates a clean (DW) and concentrate water (CW) discharge [51]. As with other similar thermal systems, the concentrate water’s fate is underground well injection in Ohio. In other words, although about 80% of the feed solution has been purified, the remaining 20% must be disposed. The system is, nonetheless, effective.

AltelaRain® dewvaporation systems are currently seeing use in PA. As of

Figure 2.6 An Aqua-Pure mechanical vapor recompression NOMAD unit [75].
November 2011, four modules operated by Clean Streams, LLC, in Williamsport, PA, were treating about 106,000 gallons of flowback fluid per day (400 m³ per day) [76]. Total brine disposal cost is $4.53/bbl for this system in PA – slightly less than the nearly $5/bbl estimate by Altela, Inc. [25, 51]. The four small modules can process water at an average rate of 343.4 gallons per day (1.3 m³/d) each. According to Altela, Inc.’s website, energy use for their newest dewvaporation system is 1.0 kWh (3.6 MJ) per barrel treated [77]. If “treatment” is recovering 80% of the influent as clean water, this corresponds to 0.028 MJ/kg.¹⁸ In 2012, Altela, Inc., in conjunction with ACI Energy, Inc., and Casella Waste Systems, Inc., opened two hydraulic fracturing wastewater treatment facilities in Pennsylvania – one in Clarion and one in McKean County [78].

What does not seem well-established is the AltelaRain® system’s performance under high TDS load. The 2011 report gives various TDS values – one of 35,000 mg/L and the other of 195,000 mg/L [51]. For the higher TDS load, the system had a 49% reduction in treatment efficiency. The Colorado School of Mine’s, 2009 brief review gives the applicable TDS influent feed a 40,000-60,000 mg/L range – which is quite low [66]. Igunnu and Chen’s 2011 paper affirms 60,000 mg/L TDS as the also influent salinity concentration of the process [27]. Consequently, this process’s true applicability to produced brine and flowback wastewater may be questionable.

Unfortunately, unlike the AltelaRain® system, accurate, detailed, and reviewed data on similar, proprietary, industrial units is scarce to non-existent. A good example is Layne Energy Company’s evaporation system called EVRAS (EVaporative Reduction And Solidification). According to Layne, EVRAS uses waste heat from a gas processing plant to evaporate all the

¹⁸ See footnote 17.
water from flowback brine, leaving only the crystalized solids behind [25]. The company claims that the system is economic and TDS-insensitive; however, virtually no meaningful data is publicly available [79].

2.5.3.4 Thermal Evaporation Problems

There are several problems with treating oil and gas wastewater using thermal methods. First of these is fouling from organic residue and inorganic chemical precipitates [17]. Crystalline deposits on heat transfer surfaces in boiler systems typically have very low thermal conductivity, decreasing system efficiency [80]. Even in seawater thermal evaporators, the seawater is frequently chemically pretreated and deaerated to prevent foaming and scaling within the evaporator [43]. Generally, thermal distillation and evaporation is used for feed waters with TDS concentrations between 40,000-100,000 mg/L [13]. The highest possible influent TDS concentration the author has seen is given by Gaudlip, et al., of 150,000 mg/L; but, for this value, these authors cite no source nor give any justification [17].

The second problem is capital cost [25]. Until the production of multi-stage units, thermal distillation was not considered energetically cost-effective for treating produced water [46]. To address fouling, scaling, and corrosion concerns, newer brine evaporators are produced as modular, disassembling (for cleaning) units fabricated with costly corrosion-resistant metals [17]. Further, to avoid breakdowns, mechanically-intensive mechanical vapor compression systems must use costly, quality components (i.e., compressors, pumps, etc.). Also, it must be considered that when exposed to hypersaline brines at elevated temperatures (where the metals must conduct the thermal energy required for solvent evaporation) these inert metals will corrode.
Finally, thermal evaporative units always have some highly-concentrated, liquid discharge. True, they reduce influent volume, but they do not distill 100% of the feed. For example, Dores, et al., report that the Mukhaizna Water Treatment facility in Oman uses thermal evaporation via a mechanical vapor compression system to concentrate produced brines from petroleum production processes, but the post-process wastewater is disposed of in underground injection wells [26]. Consequently, although thermal evaporative systems can reduce the wastewater volume, they cannot completely remediate it.

2.6 Unconventional Wastewater Treatment Options

Presently, unique membrane technologies are perhaps the most unconventional oil and gas wastewater treatment technologies. New Logic Research, Emeryville, CA, markets a unique membrane treatment process called Vibratory Shear Enhanced Process capable of treating flowback and produced brines [81]. As shown in Figure 2.7, by vibrating the membrane, this process can accommodate wastewaters with TDS concentrations up to 100,000 mg/L without fouling [81]. The process uses nano, ultra, and microfiltration membranes to pretreat the wastewater before reaching the vibrating reverse osmosis membrane element. A report on Vibratory Shear Enhanced Process technology gives the technology energy requirement as 0.23 MJ per kilogram of clean water produced – a highly competitive energy value [82]. Because of the

![Figure 2.7 Conventional membrane process shown at left, compared to the Vibratory Shear Enhanced Process, which prevents flux loss due to membrane plugging [85].](image)
favorable, fouling-reduction effect of the shear at the vibrating membrane surface, this type of technology is also touted as being capable of treating reverse osmosis retentate brine [83].

Another novel membrane use is membrane distillation. Minier-Matar, et al., successfully used to membrane distillation pilot units to treat a feed with 70,000 mg/L TDS [84]. The feed, however, had to be pre-treated with granular activated carbon to remove organic contaminants and particles [84]. This pilot system review did not include any information on energy requirements.

2.7 Summary

In briefly reviewing the brine remediation techniques currently available to the oil and gas industry, it becomes readily apparent that influent TDS concentration is a common limitation. Table 2.3 clearly shows this. While successful oil and gas wastewater treatment commonly requires a series of operations, what can the industry do with a brine TDS concentration exceeding 150,000 mg/L [86]? In 2010, the value of the oil and gas waste water treatment industry was estimated at $2.5 billion, but does such an industry truly exist [41]? There are a few National Pollutant Discharge Elimination System (NPDES) accredited industrial plants that offer to remediate hydraulic fracturing waste water, but are they simply treating the cleanest wastewaters [17]? The present situation was well-described by Kargbo, et al., when they wrote, “New and cost-effective technologies that treat wastewaters with TDS exceeding 200,000 mg/L are needed” [13].

<table>
<thead>
<tr>
<th>Separation Process</th>
<th>Range of Source Water TDS Concentration for Cost-Effective Application (mg/L)</th>
</tr>
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<tbody>
<tr>
<td>Distillation</td>
<td>20,000-100,000</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>50-46,000</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>200-3,000</td>
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<tr>
<td>Ion Exchange</td>
<td>1-800</td>
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2.8 References


CHAPTER 3: LITERATURE REVIEW

3.1 Introduction

The research related in this work employed a super-charged pulsed jet combustor to separate dissolved solids from water. The specifics of this proprietary pulsating combustor and its experimental setup can be found in Chapters 5-7 of this thesis. Since no unit or process like this one has ever been developed before, the team sought other similar technologies to which this pulsating combustor and salt-water separation process may be akin.

This super-charged pulsed jet combustor may be related to pulsating combustors, most commonly referred to as “pulse combustors,” and sometimes as “pulsed combustors.” The differences between these two types of pulsating combustors will be discussed in the following section. Furthermore, a detailed review of pulsating combustors is also included in this chapter.

The experimental process by which the super-charged pulsed jet combustor is applied to separate dissolved solids and water may involve spray drying as one of the phenomena that occur. Consequently, the pertinent background and specifics of spray drying and spray drying using pulsating combustors are also discussed in this chapter.
3.2 Pulsating Combustors: Pulsed and Pulse Combustors

In differentiating between pulse and pulsed combustors herein, the team has adopted the nomenclature of Putnam, *et al.*, [1]:

“Pulsed combustors, as distinct from pulse combustors, are...defined as combustors that are purposely fired at frequencies considerably below the natural acoustic frequencies of the combustion system or that fire on their own at some much lower frequency. Pulsed combustion refers, therefore, to non-steady combustion initiated by either externally arranged timed fuel injection and/or ignition or by process other than those conforming to the normal mode of operation described herein as pulse combustion.”

The team therefore defines a pulsed combustor as being a pulsating combustor that uses an externally-controlled, mechanically-actuated valve that regulates fuel and/or air flow into the combustion chamber of the unit. In contrast a pulse combustor is one that has no externally-controlled, mechanically-actuated fuel and/or air valve, and the flow of fuel and/or air into the combustion chamber is governed by the acoustical and/or geometric nature of the combustor and/or by independently-actuated, mechanical valves that are actuated by changes in pressure (e.g., spring-loaded, flapper valves).

The research related in this thesis employed a pulsating combustor called a super-charged pulsed jet combustor. It relied on an externally-controlled, mechanically-actuated, rotating valve to regulate the frequency at which the compressed air was fed into the unit’s combustion chamber. The rotational frequency of this valve should have established the frequency of the pulses of combustion [1]. This externally-controlled, mechanically-actuated, rotating valve also provided the current (via magnets on a flywheel, attached to the valve, which rotated past a small-engine magneto) to a spark plug in the combustion chamber, which ignited the fuel air mixture within.

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19 Putnam, *et al.*, however, do not offer a succinct definition of “pulse combustion.” The reader is encouraged to consult Putnam, *et al.*, and all the other sources cited in this chapter to synthesize their own understanding of the complex, thermoacoustic “pulse combustion” phenomenon.
3.2.1 Traditional “pulse combustion” and classical “pulse combustors”

According to Webster’s dictionary, combustion is the act or instance of burning. At its most fundamental level, pulse combustion is the cyclical burning of fuel, as a continuous process. In other words, combustion occurs, followed by a period of inactivity (i.e., quiescence), which is again followed by combustion, and so on.

In fact, all combustion engines pulse. In conventional combustors, however, these oscillations are eliminated or dampened as much as possible. For example, baffles in a car’s muffler dampen and homogenize the noisy pulses of exhaust coming from the internal combustion engine. In pulse combustors, however, achieving and maintaining continuous oscillation between combustion and quiescence is the goal [2].

Physically, classical pulse combustors appear simple. They can be constructed from a single piece of shaped, sheet metal, or from several joined together. In general, as shown in Figure 3.3, a pulse combustor has provisions for air and fuel intake, an ignition source, a combustion chamber, and an exhaust tail pipe.

According to the literature, there are three types of classical pulse combustors: Helmholtz, Schmidt, and Rijke [3, 4]. The basic difference in classification between each of these three types is acoustic operation [4]. Beyond acoustic operation, a pulsating combustor can be further categorized by the way air enters its combustion chamber. As shown in Figure 3.1, classical pulse combustors are either valved or valveless [5].

Figure 3.1 A mechanically-valved (spring-loaded, flapper-type valves) pulse combustor (top), versus an aerovalved (or valveless) pulse combustor (bottom) [1].
Valveless pulse combustors are commonly referred to as “self-aspirating” or “aerovalved.” Despite not requiring valves, properly designing the body of aerovalved pulse combustors is quite difficult since they regulate air inflow via their geometric shape. Thus, they are made from several precisely formed sheet metal pieces – usually two venturi tubes with a reinforced combustion chamber between them, a fuel delivery line, and spark plug [6].

Some pulse combustors utilize independently-actuated mechanical air supply valves [7, 8]. Independently-actuated mechanical valves open and close based on the pressure inside the combustion chamber (i.e., when combustion occurs, the pressure spikes, closing the valves, shutting off the air supply; after combustion temporarily ceases, the pressure drops, and the valves spring open). A common example of the physical mechanism that controls an independently-actuated mechanical valve is a spring. (These differ from externally-controlled, mechanically-actuated valves; an example of which is an externally-controlled rotating valve that controls air and/or fuel flow, and is spun by a motor.)

Based in thermoacoustics, the principles of classical pulse combustion are complicated, complex, and perhaps not well understood [9]. The basic operation of a pulse combustor, however, is simple to describe and understand.

![Figure 3.2 One pulse combustion cycle as shown in four phases [1].](image-url)
Using Schlieren photographs\textsuperscript{20} of an aerovalved pulse combustor, Keller, \textit{et al.}, identified and outlined three distinct stages of pulse combustion: (1) injection – under pressure, fuel and air enter the combustion chamber; (2) rapid combustion – the pressure increase shuts off the flow of reactants, and the products are expelled out the body; and (3) quiescent period – the pressure within the combustion chamber drops, setting the stage for more fuel and oxidant to be drawn in, and combustion products thoroughly mix as they travel down and exit the end of the tailpipe \cite{2}. Other basic descriptions of the pulse combustion process differ slightly from the account in Keller, \textit{et al.} (\textit{e.g.}, see Figure 3.2); however, they are all similar.

Once initiated, pulses of combustion occur cyclically at an established frequency (reported frequencies range from 20 to 250 Hertz [abbreviated “Hz”; units are “s\textsuperscript{-1}”]) and will continue as long as the supply of fuel and oxidant is adequate \cite{4, 5, 10}. In valveless systems or those using flapper-style independently-actuated mechanical valves, it is not so clear what drives the combustion cycles – although combustion frequency has been shown to be dependent on tailpipe length\textsuperscript{21}, combustion chamber volume, and gaseous fuel supply pressure \cite{2, 11, 12}.

In general, if the pulses of combustion are not forced, and the energy released by them exceeds the amounts lost through dissipation (\textit{e.g.}, through the exhaust gas), radiation, and heat transfer to energy sinks (\textit{e.g.}, the combustor body; a cooling jacket; etc.), the thermodynamic requirement for continuing combustion is met \cite{13}. Physical objects and/or bodies have some inherent natural resonant acoustical frequency. When the timing of the energy addition precisely

\textsuperscript{20} “Schlieren” is the German word for “streaks,” and refers to the gradient disturbances (\textit{e.g.}, temperature or velocity change, or dissimilar materials mixing) of inhomogeneous transparent media (\textit{e.g.}, solids, liquids, and gases). Thus, a Schlieren photograph is a picture of light rays bent in any direction other than the normal “z” direction caused by a gradient disturbance \cite{77}.

\textsuperscript{21} Of the pulse combustion parameters affecting operating frequency, this tends to be the most investigated, and it is well-documented that the frequency of combustion pulses increases as tailpipe length decreases \cite{11, 51, 65}.
matches the resonant frequency of the combustor, the amplitude of the following combustion cycle can be driven up, per Rayleigh’s Criterion [9, 14].

### 3.2.2 More on Deliberately Pulsed Combustion

Although all types of pulsating combustors have been used industrially, mechanically-valved systems seem preferred [1, 15]. Some of the significant advantages of mechanically-valved, versus aerodynamically-valved, pulsating combustors may be: easier operational control, improved mechanical robustness, ease of development, compact design, noise reduction, strong acoustic gas flow oscillations, and better air-fuel flow rate control [1, 4, 8, 15, 16].

Mechanically-valved systems, however, may have some disadvantages. Because they are often located in close proximity to the combustion chamber, the valves are exposed to high temperatures, causing wear; also, an air blower or compressor is required to deliver oxidizer [9, 15]. Further, for the pulses of combustion to match the inherent acoustical resonance of the combustor body,\(^{22}\) it is critical that rotating valves open precisely when pressure in the combustion chamber is lowest [4, 6]. This may be difficult to accomplish in a pulsating combustor with an externally-controlled, mechanically-actuated valve. As Putnam, et al., noted, “[It is] doubtful that the timing [of a rotary-valved pulse combustors] would normally be optimum for best performance without some sort of feedback mechanism” [1]. Because pulsating combustors operate at very high frequencies and temperatures, fulfilling this feedback requirement is difficult, further complicating the use of mechanically-actuated, externally-controlled, rotary-valved, pulsating combustors.

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\(^{22}\) A discussion of acoustical resonance of metal bodies is beyond the scope of this work. The work of Rijke is traditionally cited as being the initial, defining study on this topic; see [76].
3.3 The History of Pulsating Combustors

The history of pulsating combustion begins in 1777 when Byron Higgins observed hydrogen flames “singing” in a tube at its resonant frequency [8]. Eighty-two years later, Dutch physicist and professor Pieter Rijke found that strong acoustic oscillations could be created by positioning a heat source in the lower half of an open-ended vertical tube [8]. In 1906, the first functioning classical pulse combustor was made and patented by V. Karavodine [1, 17]. This particular design was built to generate thrust for propulsion, and is therefore called a “pulse jet.” Also in 1906, Frenchman, Esnault-Pelterie, also patented a mechanically-valved pulse jet [1]. More well-known, however, than either Karavodine or Esnault-Pelterie’s designs is the valveless pulse jet engine patented by French inventor G. Marconnet, in 1909 [1].

Until the Second World War, pulse jets were a novelty. That changed, however, with the Argus As 014 pulse jet engine. Developed by German engineer Paul Schmidt, this pulse jet powered the Nazi’s V-1 flying or “buzz” [23] bomb, shown in Figure 3.3 [1, 8]. A precursor to unguided missiles, this weapon was crude but relatively effective. Being inexpensive and burning low-grade petroleum-based fuels, the Germans mass-produced V-1’s to attack Great Britain’s cities [18]. Although by using a pulse jet the Germans benefited from several inherent pulse combustion advantages (i.e., low-cost, insensitive to fuel quality, etc.), they also had to contend with its drawback: minimal thrust. The V-1 required an external power source to become airborne and had

Figure 3.3 The V-1 flying bomb; once launched, it was propelled by the Argus As 014 pulse jet [74].

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23 This weapon was given this nickname because of the apparent “buzzing” sound that came from the pulse jet engine, in flight.
a low flight velocity [1]. It was so slow that Allied fighter planes and anti-aircraft batteries could shoot it out of the sky before it reached its target.

3.4 Common Applications of Pulsating Combustors

As previously noted, interest in pulsating combustors stemmed from the desire to use them as thrust-generators for propulsion. At the end of the Second World War, however, the advent of the turbojet reduced interest in the technology [2]. In the 1970’s, however, rising fuel prices and growing air-quality concerns reignited research into fuel-efficient, low-emission pulsating combustors for domestic and industrial use [2, 8]. This renaissance led to pulsating combustors being used for industrial drying, steam generation, acoustic and vibro-acoustic heated surface cleaning, bitumen liquefaction, small particle coagulation, and air heating and ventilation [1, 7, 19, 20]. In the USSR, they were even used as soot blowers [19].

Today, several companies claim to use pulsating combustors for industrial drying [21]. A Dutch thermodynamic application consulting firm, DLF Sustainable, designs a variety of drying systems using pulsating combustors [22]. In the United States, Pulse Combustion Systems™ (Payson, AZ) provides custom-built spray drying systems using pulsating combustors, and offers product drying trials on their pilot-scale systems [23]. In their manufacture of specialty food products, Berghausen Corporation (Cincinnati, OH) employs spray drying systems that use pulsating combustors.

Figure 3.4 The Hosokawa Bepex Corp. 80-150 Hz, 300 kW rotary-valved, pulse combustor drying system [8].
The Hosokawa Bepex Corporation (Leingarten, Germany) makes food processing equipment and offers dryers that use pulsating combustors (an example is shown in Figure 3.4) [8, 16]. Pulse Drying Systems, Inc., (Portland, OR) offers drying services via mobile and fixed industrial pulsating combustion units (Figure 3.5 shows one of their mobile industrial drying units) [25]. Fulton Thermal Corporation (Pulaski, NY) manufactures water boilers that employ pulsating combustors as the heat source [26].

3.5 Drying

As an adjective, Webster’s dictionary defines “dry” as, “Free or relatively free from a liquid and especially water; not being in or under water; lacking precipitation or humidity.” As an adverb, “drying” means, “To remove water or moisture from.” When remediating water-based liquid solutions, evaporation is generally avoided due to the high energy requirement. Instead the focus is on separating the solvent and solute while maintaining the liquid state of the solvent water. When the solute concentration is high, however, is this approach still valid?

Consider a salt (NaCl) and water brine: The solubility of halite (NaCl) in pure water at 20°C (68°F) is 359 g/L (2.996 lb/gal). At this temperature, the density of water is 999.97 g/L (8.345 lb/gal). Therefore, if a 20°C water-based brine is supersaturated with respect to NaCl, 26.42% of the solution’s mass is entirely solid. With such a high salt content, separating the dissolved solid ions from the solvent water without changing its phase is difficult, and becomes even more so if the solution’s chemistry is further complicated by the presence of other compounds (e.g., organic molecules, various ionic salts, etc.).
Drying is a simple technique for separating solids and water. Drying, however, involves changing the phase of solvent water and is therefore an energy-intensive process [6, 27]. Zbiciński, et al., call drying, “One of the most harmful [processes] to the environment and [most] energy demanding unit operations in chemical engineering” [28]. Because of this, any thermodynamic improvements that can be made to drying processes are relevant and important.

3.6 Spray Drying

A common method for rapidly dehydrating a solid-liquid solution is spray drying [29]. Dating to the 1870’s, spray drying is an aerosol-drying method, capable of producing very fine, dry powders [30, 31]. In his 1985 Spray Drying Handbook, Masters wrote that spray drying is, “[T]he transformation of feed from a fluid state into a dried particulate form by spraying the feed into a hot drying medium...a one-step, continuous particle-processing operation” [31]. Common examples of commercial products produced using spray drying are chemicals, pharmaceuticals, and also food products like dairy powder and dried eggs [29, 31, 32].

The spray drying process begins with the atomization of a solution into an environment favorable for solvent evaporation. Typically, a nozzle is used to complete this step. (Atomization will be discussed in the following section, Section 3.7.) Droplet size is controlled by the aerosol generator (i.e., the atomizing nozzle; also called an “atomizer”) and by the

Figure 3.6 A typical spray drying process layout [35].
characteristics of the solution (e.g., density, surface tension, viscosity, etc.) [33]. The process has
two key stages: drying and particle formation [30]. First, the droplets approach their wet bulb
temperature [30]. Once the droplet has reached this level of internal thermal energy, the mass of
the droplet rapidly decreases, as solvent evaporates. Eventually, the solids within the shrinking
droplet begin to crystalize, and drying continues until only dehydrated product remains [30].

In industrial spray drying, the key consideration is particle formation. Although droplet
drying is modeled as evaporation from a free liquid surface, solvent molecules within the droplet
may become enveloped by crystalizing solids, thus decreasing the drying rate (compared to that
of a pure liquid) [33]. This behavior is controlled by altering the temperature of the drying gas to
create specific particle morphologies. For example, drying in a very hot gas increases the
solvent evaporation rate so that it exceeds solvent diffusion inside the droplet, creating a high
concentration gradient within the droplet, forming large, hollow particles [30]. Conversely, low
drying chamber temperatures result in small, fine, solid particles [30].

Conventional spray drying is expensive – both in energy and capital costs. Using
convective heat transfer to volatilize water molecules requires between four and five mega Joules
(MJ) of energy per kilogram (kg) of water evaporated – more than twice water’s latent heat of
vaporization

\[ \Delta H_{\text{vap}} \]

[31, 34]. Spray drying also produces large volumes of low-grade waste heat, the
recovery of which is usually considered to be too expensive [31]. Traditional spray dryers are
also physically large, expensive to fabricate, and costly to install [31]. Consequently, the use of
spray drying is typically limited to the production of thermally-sensitive materials where the
value of the produced, dry product exceeds the required energy and capital costs.

24 The heat (or “enthalpy”) of vaporization (\( \Delta H_{\text{vap}} \)) of a liquid substance represents the energy at which its molecules
transition from the liquid to the gas phase, without an increase in temperature [54, 75]. Therefore, the heat of
vaporization for liquid water at a specific temperature and atmospheric (or overburden) pressure represents the
minimum amount of energy required to cause evaporation.
3.7 Atomization

Crucial to conventional spray drying is the atomization of the liquid feed solution [31, 35]. The term “atomization” does not imply that a molecule is broken down into its constituent atoms. Rather, it means to turn a bulk liquid into a mist of small droplets [31]. In Atomization and Sprays, Lefebvre defined atomization as, “[The process] in which a liquid jet or sheet is disintegrated by the kinetic energy of the liquid itself, or by exposure to high-velocity air or gas, or as a result of mechanical energy applied externally through a rotating or vibrating device” [36]. The purpose of atomization is to achieve the smallest droplet size possible, thereby increasing the specific surface area of the liquid to improve mixing and vaporization rates [37].

Atomization has two stages: primary and secondary droplet breakup [36]. Primary atomization is the initial disintegration of the bulk liquid phase. It is typically achieved using a nozzle (e.g., a garden hose nozzle, shower head, spray-paint can head, fuel injector in a car engine, etc.). In general, nozzles are based on the laws of momentum conservation: By reducing the cross-sectional area through which a liquid flows, the velocity of the fluid traveling through it increases. When the high-speed liquid exits the orifice, it enters the relatively low-velocity, ambient air (or it encounters an inanimate, rigid object in its path) and it “shatters” or “atomizes” into droplets.

After this “primary breakup” or “primary atomization,” secondary atomization continues to reduce droplet size until a stable condition is achieved. This secondary breakup occurs because the droplets resulting from primary atomization are highly unstable [38]. Even slight pressure waves (e.g., sound waves) acting on newly-formed droplets can cause secondary atomization [39].
The breakup of a bulk liquid is complicated and significantly affected by liquid and gas properties [36, 37]. The primary forces governing liquid droplet breakup are: inertia, surface tension, and viscous and aerodynamic drag forces [40]. The breakup of the bulk liquid phase is like a game of tug-of-war: Surface tension and liquid viscosity seek to keep the bulk phase together, while external disruptive forces act to break it apart [36].

For predicting droplet breakup, two important values are the Weber number (We), and the Ohnesorge number (Oh). For multiphase flow (i.e., liquid being atomized into a surrounding gas), the Weber number is a ratio of the drag (or disruptive) forces acting on a droplet to its surface tension force \((We = \frac{\rho \, \mathcal{d}_0 \, u_0^2}{\sigma})\) [41]. As shown in Figure 3.2, the Weber number can be used to predict droplet break up behavior. At high Weber numbers, large droplets rapidly flatten in a plane perpendicular to the source of the gas flow disturbance (which is causing the atomization) and then shatter into microdroplets [8].

The Ohnesorge number is the ratio of a liquid’s viscous force to its surface tension \((Oh = \frac{\mu_L}{[\rho_L \, \mathcal{d}_0 \, \sigma]^{0.5}})\) [41]. A high Ohnesorge number indicates a highly viscous liquid, which implies less droplet deformation, or more energy required for droplet deformation. Because droplet deformation is the first step in atomization, when the Ohnesorge number is large a greater disturbance (i.e., a higher We) is required to achieve atomization [38, 42].
Figure 3.7 Droplet break up characterized by Weber (We) number range [41].
Although the atomization induced by physical nozzles is well-understood and calculable, the use of a physical nozzle with a highly viscous or abrasive solution implies eventual erosion, which will gradually increase droplet size. In spray drying, as droplet size increases, the efficiency of the drying unit decreases. Therefore, an alternative method for inducing atomization is to use nozzle-less atomization by introducing a low-momentum, fluid flow into a high-momentum gas flow.

3.8 Pulsating Combustors as Dryers

Initially, combustors that operated in a pulsating mode were pursued as potential propulsion technologies (i.e., “pulse jets”). Because they generate little thrust, however, pulse jets have been largely abandoned [43]. Although there are many applications for pulsating combustors, a very common and successful use has been as part of the spray drying process [44].

Conventional spray drying has two inherent drawbacks. First is the low conductive heat transfer rate from the mildly turbulent, heated air to the droplet. Second is the potential for eventual erosion and clogging of physical atomizing nozzles. Using a pulsating combustor as part of the spray drying process can overcome both of these issues. The combustion oscillations produce high-temperature, high-velocity, pulsating exhaust gas jets, which can simultaneously atomize viscous solutions and then evaporate solvent [8].
3.8.1 Convective Heat Transfer

As discussed in Chapter 2, non-condensable gases – like air and CO2 – have low heat transfer efficiencies [45]. This can make conventional convective air drying unappealing [46]. The hot exhaust from pulsating combustors, however, is widely cited as being so turbulent that the convective heat transfer coefficients therein exceed that of their steady-state combustor counterparts [19, 47]. This can make them two to five times more efficient when used as dryers [48]. There is even the claim that when compared to steady-state combustors, pulsating combustors intensify heat transfer by 100-300% in laminar, hot gas flows and by 20-30% in turbulent regimes [19]. More moderate improvement values, however, are commonly reported (e.g., Dutko, et al., found they evaporated 25-30% more water in a drying chamber, when the energy source came from a pulsating versus steady-state combustor) [49]. This documented performance improvement is due to enhanced convective heat transfer inherent in the nature of pulsating combustion.

Convective heat transfer is based on Newton’s Law of Cooling, as shown in Equation 3.1 [50]. A particularly important term in Equation 3.1 is the convective heat transfer coefficient \( h_c \), which has units of \( \text{W m}^{-2} \text{K}^{-1} \). This proportionality coefficient can predict drying behavior; however, it is often system-dependent and must be empirically determined.

\[
\dot{Q} = h_c A (T_s - T_\infty)
\]

Equation 3.1 Newton’s Law of Cooling, where \( \dot{Q} \) is the rate of heat transfer, \( h_c \) is the convective heat transfer coefficient, \( A \) is the area, \( T_s \) is the surface heat temperature, and \( T_\infty \) is the bulk fluid temperature [50].
dimensionless numbers are the Prandtl number (Pr; the ratio of kinematic viscosity to thermal diffusivity) and the Reynolds number (Re; the ratio of inertial forces to viscous forces). These are introduced here, because they are discussed more in the following section, Section 3.8.2.)

Convective thermal energy transfer for solvent (i.e., water) vaporization may be desirable when separating dissolved salts and water, at high ionic strengths. Although thermal energy transfer is more efficient via conduction than convection, corrosion is a serious and common concern in brine treatment systems that rely on conductive energy transfer for solvent evaporation [52, 53]. The transfer of thermal energy from a metallic surface to the harsh, saline brine makes corrosion inevitable for all but the most noble metals or alloys (e.g., copper, nickel, chromium, zinc, monel, etc.), and these are expensive [54-56]. In a similar vein, fouling and scaling are two other serious and common issues that conductive brine treatment systems face, as crystalline deposits on heat transfer surfaces tend to have an insulating effect are reduce conductive heat transfer efficiency [55, 57, 58]. The inevitability of corrosion and scaling coupled with the high cost of solving these problems makes convective drying appealing for dehydrating hypersaline brines.
3.8.2 Pulsating Waves

Combustors that deliberately operate in pulses typically produce high velocity (± 100 m/s), rapidly varying (20-500 Hz), mildly pressurized, jets of hot gas [4, 59]. These phenomena enhance convective heat transfer rates in two ways. First, the rapidly varying amplitude of gas pressure creates a highly unstable environment around the droplet, increasing the solvent evaporation (i.e., drying) rate [48]. Second, the extreme gas turbulence improves heat transfer efficiency [45]. As shown in Figure 3.8, in a pulsating gas flow, the high-humidity gas layer that surrounds and insulates the surface of liquid droplets is continually stripped away, accelerating solvent evaporation [7]. The heat transfer coefficient is directly affected by the continual disruption of the boundary layer between the hot gas and a drying droplet [8]. Ain, et al., wrote, “In the pulsating flow, the droplet surface loses stability and gets covered with pulsating waves, which…enhance[s] heat transfer from the gas to the droplet” [60].

Extensive research has demonstrated the beneficial effects of pulsed air flow on convective drying rates. Investigating droplet evaporation from a solid surface, Ain, et al., showed that when exposed to a pulsating hot air flow, solvent evaporation rate increased [60]. Although these authors found 50 Hz to be the optimal drying gas pulsation frequency for their system (see Figure 3.8). Within the exhaust from pulse combustion, the insulating surface boundary layer is stripped in one direction (to the left), then a very short time later, to the other (to the right); and this constant oscillation continues [8].
Figure 3.9), their main conclusion was that pulsating hot
gas flow enhanced droplet evaporation at any
frequency. (For the system used by Ain, et al., at 50 Hz,
the velocity distribution was most deformed. This
frequency is on the low end of typical operating
frequencies of pulsating combustors; however, the
concept still applies.)

Nomura, et al., evaluated the water evaporation
rate from the surface of a wetted, refractory brick
(porosity = 71%) placed in the tailpipe of a pulsating
combustor [12]. They found that when the brick was
wet but water was evaporating, the frequency of the
combustor was unaffected, but the form of the exhaust
gas wave changed. They also found that the drying rate
was nearly five times greater than the drying rate when a continuous combustor (e.g., a heater
generating a steady stream of hot air) was used as the heat source for water evaporation. Using
the Laser Schlieren Photographic Method, Nomura, et al., demonstrated that this increase in
drying rate was caused by the stripping the thermal boundary layer (as previously discussed and
shown in Figure 3.8), which was achieved in the exhaust from a pulsating combustor.

Historically not all studies on the effect of pulsating gas flows on convective heat transfer
rates show an improvement. Because of this Al-Haddad and Al-Binally conducted a thorough
investigation on the topic [46]. They used a low-pressure, experimental apparatus to vary the
Reynold’s number (Re) of a pulsating (5-60 Hz) hot (50-100°C) gas flow from 1,000 to 40,000.
The authors found that when $\text{Re} \omega' > 2.1 \times 10^5$ (where $\omega'$ represents pulsation frequency), convective heat transfer was significantly enhanced. Al-Haddad and Al-Binally did not explore the effects of pulsation amplitude because Al-Haddad had previously established that in low pressure systems, amplitude fluctuation did not significantly affect the heat transfer coefficient.

Dec and Keller studied the effects of exhaust gas wave frequency, amplitude, and mean flow rate on heat transfer rates in the tailpipe of a pulsating combustor [51]. As shown in Figure 3.10, they found that the Nusselt number was higher in a pulsating than in steady-state combustion gas jet. In their experiments, Dec and Keller demonstrated that Nusselt number was independent of the combustion frequency, but varied linearly with the root-mean-squared combustor chamber pressure. Furthermore, this pressure was directly related to the velocity oscillation amplitude of the exhaust gas. At most,
Dec and Keller found the Nusselt number from pulsating combustion could be 2.5 times higher than that of steady (but turbulent) combustion.

As shown in Figure 3.10, Dec and Keller reported little difference in heat flux along the combustor tailpipe, for both pulsing and steady combustion [51]. Hanby found a similar result [47]. In his research, Hanby noted that oscillating pressure amplitude decreased along the centerline axis of the tailpipe of his pulsating combustor, but the heat flux remained relatively constant. His hypothesis was that this was caused by increasing particle velocity (and, therefore higher heat transfer coefficient) which negated the dropping gas temperature along the length of the tailpipe.

Although it is generally accepted that pulsing gas waves enhance convective drying performance, there are limitations. First, every system is unique and may not be comparable to any other (particularly when trying to compare pulsating combustors to more traditional steady-state combustors). Second, even in successful experiments, investigators found a limit beyond which there was no enhancement of the convective heat transfer rate. For example, in their research Wu and Mujumdar found a pulse amplitude beyond which droplet drying rate did not appreciably improve [59].

It is important to note that heat transfer is not independent of the thermodynamics of the combustor. In other words, the transfer of heat from the hot exhaust gases of a pulsating combustor can directly influence and/or alter the operating principles of the combustor [51]. This may be why there are reported limits beyond which the drying performance of particular experimental pulsating combustors does not improve.
3.8.3 Bulk Fluid Atomization without a Nozzle

The atomizing capabilities of pulsating combustors are well-documented [48, 61]. In a 2002 technology review article, Zbicinski wrote, “Pulse combustion drying systems can be used to dry a wide range of materials, including low and high viscosity liquids, pumpable pastes, all non-cohesive filter cakes (and most cohesive ones) and many powders and granules” [8]. According to Ozer, slurries with viscosities up to 1,600 centiPoise (cP), and solutions with viscosities up to 300 cP can be readily atomized using a pulsating combustor [16]. As discussed in Section 3.7, sudden changes in momentum can induce atomization. Because pulsating combustors generate such powerful, turbulent exhaust gas jets, liquid streams introduced into these regions instantaneously atomize – no nozzles required [6, 16].

Atomization, however, requires energy. Introducing bulk solution into the exhaust from a pulsating combustor dampens the oscillating gas pressure amplitude [7]. Because atomization increases fluid entropy, energy comes from the exhaust jet gas. Consequently, some spray dryers that use pulsating combustors also utilize nozzles to induce primary atomization [6]. As previously noted, however, such systems may run the risk of potentially clogging the nozzle, when drying slurries or solutions with high solids concentrations.

3.8.4 Acoustic Energy

Pulsating combustors generate sound. Their noise is the combined product of (1) the detonating character of combustion; (2) the vibrations of the combustor body; and (3) the velocity difference between the exhaust gases from the combustor and the surrounding ambient air [8]. Generally, noise levels rise as the oscillating pressures of the exhaust gas increase [1].
Although considered harmful in other combustors, these “acoustic combustion instabilities” are beneficial and necessary in pulsating combustion [2]. Acoustical energy from a pulsating combustor can benefit a spray drying process in two key ways: (1) by inducing secondary atomization; and (2) by creating localized areas of low-pressure. As discussed in Section 3.7, following primary atomization, the resultant liquid droplets are barely stable, and even sound pressure waves can initiate secondary atomization. This reduction in droplet size increases the evaporation rate of the solvent by increasing the heat transfer rate from the hot gas to the smaller droplet [39].

Sound waves are pressure waves moving through a fluid (typically air). At lower pressure, the molecular energy required to evaporate water is reduced compared to at normal or higher pressures. These localized sequential drops in pressure, caused by the acoustic pressure waves from pulsating combustion, may cause water to flash-evaporate, enhancing drying efficiency [62].

Although possibly beneficial, acoustical energy is noise. It is well known that pulsing combustors are very noisy [13, 19]. While steady state combustors usually emit sound intensities of 85-100 decibels (dB), pulsating combustion noise levels are almost always over 100 dB – some reaching 180 dB [6, 19, 48, 63, 64]. High sound intensity limits the industrial application of pulsating combustors. According to the 29 Code of Federal Regulations (CFR), Part 1910.95, a worker cannot be exposed to sound in excess of 90 dB for over eight hours per day. For this reason, Kudra and Mujumdar, say that “the major disadvantage of pulse combustion systems” is the noise they generate [4].
The noise problem, however, is not insurmountable [1]. Perhaps the most common method of providing acoustic reduction or termination is by attaching the tailpipe of a pulsating combustor to a decoupling chamber [13, 51]. When using a pulsating combustor as part of a spray drying system, the drying chamber can fulfill this role [4, 7, 65]. An added benefit of such an array, however, is that if the pulsating combustor excites the inherent resonant frequency of the drying chamber, the pressure waves from the combustor are increased within the drying chamber, thereby enhancing evaporative rates [48, 21]. In some systems the highly unstable resonant acoustic environment within a drying chamber (sometimes called an “applicator,” especially in this role) is considered more useful for effective solvent evaporation than the thermal energy provided by the exhaust from a pulsating combustor [4].

In addition to decoupling chambers, there are many other proven sound-reduction techniques for pulsating combustors. With two self-aspirating pulsing combustors, Giammar and Putnam found that acoustically coupling the combustion chambers of the two units noise levels could be reduced by up to 20 dB [20]. Ohiwa and Yamaguchi found that lengthening the tailpipe of their pulsating combustor by one meter reduced the sound by 5 dB [66]. Also, as previously noted, the use of mechanical valves on pulsating combustors generally reduces noise, and some mechanically-valved systems have been constructed to operate as quietly as 75 dB [6, 63]. As shown in Figure 3.11, reducing combustor power can also decrease sound intensity (however,
this may have a negative effect on drying performance) [63]. Ramanarayanan, et al., found a similar result: sound pressure level increased as more air was fed to their pulsing combustor [64].

3.8.5 Energy Efficiency

There are two metrics that are commonly used to evaluate the performance of pulsating combustion dryers. First is combustion efficiency (i.e., how completely fuel is oxidized in the combustion reaction within the burner). Second is the amount of energy required to evaporate a given water mass. This is typically reported as mega Joules (MJ) of energy consumed to evaporate a kilogram (kg) of water (i.e., MJ/kg).

Unlike steady-state combustors, pulsating combustors are recognized as attaining a high fuel-burning efficiency – 90 to 99% [19, 49, 51, 62]. One pulsing combustor in the reviewed literature was reported to be 40% more efficient than an equivalent continuous combustor, while consuming 34% less fuel [48]. The highly turbulent nature of pulsating combustion within the combustion chamber accelerates and enhances fuel-air mixing [13, 49]. This decreases the amount of air required for complete combustion, and results in more efficient air use during combustion [7, 8].

As noted by Kudra, et al., objectively comparing system efficiency between steady state and pulsing combustors is difficult because of the many disparities and variations between systems [48]. Additionally, “efficiency” is a relative term [17]. Consequently, comparing evaporative systems by the amount of energy they require to evaporate a kilogram of water is likely the most informative way to compare dryer system performances.

The latent heat of vaporization of water is 2.257 MJ are required to evaporate one kilogram (kg) of water [67]. This is the theoretical limit; the minimum amount of energy
required to evaporate a kilogram of liquid water when it is at its boiling point. Raising the
temperature of the water from about 10°C (50°F) to boiling (100°C; 212°F) adds about 0.21
MJ/kg to this required amount of energy.25

Overall, energy consumption values for experimental, pilot, and full-scale drying systems
that use pulsating combustors range from close to theoretical to just above 4 MJ/kg [4, 8, 62, 68, 69]. The highest value the author encountered was given by Putnam. For a “crude” pulsing
combustor used in a US Bureau of Mines project, Putnam reported 4.2 MJ/kg water evaporated [1].

Table 3.1 compares the performance of “pulse combustion dryers” to “conventional
dryers.” On average, conventional spray dryers use about 5 MJ/kg to evaporate water, and by
comparison pulsating combustor dryers require about 40% less energy [8, 21].

25 The approximate specific heat of water is 4.186 J g\(^{-1}\) K\(^{-1}\).
Table 3.1 Typical evaporative capacity and energy consumption (kJ/kg of water evaporated) for pulse combustion dryers and other conventional dryers [8].

<table>
<thead>
<tr>
<th>Dryers</th>
<th>Typical evaporation capacity</th>
<th>Typical consumption (kJ/kg H$_2$O evaporate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse combustion dryer</td>
<td>250–2000 kg H$_2$O/h per combustor</td>
<td>3000–3500</td>
</tr>
<tr>
<td>Conventional dryers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tunnel dryer</td>
<td>–</td>
<td>5500–6000</td>
</tr>
<tr>
<td>Band dryer</td>
<td>–</td>
<td>4000–6000</td>
</tr>
<tr>
<td>Impingement dryer</td>
<td>50 kg H$_2$O/h m$^2$</td>
<td>5000–7000</td>
</tr>
<tr>
<td>Rotary dryer</td>
<td>30–80 kg H$_2$O/h m$^3$</td>
<td>4600–9200</td>
</tr>
<tr>
<td>Fluid bed dryer</td>
<td>–</td>
<td>4000–6000</td>
</tr>
<tr>
<td>Flash dryer</td>
<td>5–100 kg H$_2$O/h m$^2$ $^a$</td>
<td>4500–9000</td>
</tr>
<tr>
<td>Spray dryer</td>
<td>1–30 kg H$_2$O/h m$^3$</td>
<td>4500–11500</td>
</tr>
<tr>
<td>Drum dryer (pastes)</td>
<td>6–20 kg H$_2$O/h m$^2$</td>
<td>3200–6500</td>
</tr>
</tbody>
</table>

$^a$ Depends on particle size.
3.8.6 Reduced Emissions

Pulsating combustors are fueled by hydrocarbons, the combustion of which releases certain harmful compounds into the air – in particular carbon monoxide (CO), nitrogen oxides (NO\textsubscript{x}), and sulfur dioxide (SO\textsubscript{x}). The USEPA lists CO, NO\textsubscript{x}, and SO\textsubscript{x} along with ozone, particulate matter, and lead as six common air pollutants [70]. Unlike other combustors, however, pulsating combustors emit minimal amounts of CO, NO\textsubscript{x}, and SO\textsubscript{x} [48].

In their 60 kW, natural-gas powered pulsing combustor, Kudra, et al., recorded NO\textsubscript{x} emissions from five to 98 ppm, and CO from three to 40 ppm [48]. According to Kudra, et al., the low emission level of 0.002-0.003 μg NO\textsubscript{x} per Joule of useful heat is “well documented” for pulsating combustion systems [48]. Severyanin cites 20-70 mg/m\textsuperscript{3} (approximately 10 to 35 ppm) as typical, empirical NO\textsubscript{x} exhaust gas concentrations for pulsating combustors [19].

There are several reasons for low concentrations of air pollutant emissions from pulsating combustors. For a unit not using mechanically-actuated, externally-controlled, rotating air and/or fuel delivery valves, during the refractory phase of the pulse combustion cycle, ambient air is sucked into the

![Figure 3.12 The calculated NO generation rate along the x-axis of Keller and Hongo’s pulse combustor, for pulsing and nonpulsing conditions [71].](image-url)
This phenomenon is sometimes called “automatic exhaust gas recirculation,” or “AEGR” [71]. The automatic exhaust gas recirculation phenomenon creates an after-burner effect, oxidizing incomplete combustion byproducts within the tailpipe [8]. More importantly, it reduces the temperature in the combustion chamber, reducing NO\textsubscript{x} formation [1, 8, 19].

The near-instantaneous combustion times in pulsating combustion further reduces NO\textsubscript{x} exhaust gas concentrations [1]. It is believed that by reducing residence time, production of NO\textsubscript{x} can be reduced [19, 72]. Kudra, et al., postulated that the oxidation of atmospheric nitrogen (“thermal NO formation”) was primarily responsible for the formation of NO and NO\textsubscript{2} [48]. Consequently, as concluded by Kudra, et al., the length of the pulsating combustor’s tailpipe and/or presence of a processing volume (e.g., a drying chamber) is significant because it increases residence time, and subsequently NO\textsubscript{x} levels.

To determine the predominant NO-reduction mechanism in pulsating combustion, Keller and Hongo performed an extensive NO-production analysis in a Helmholtz-type pulse combustor [71]. Not observing an automatic exhaust gas recirculation effect in their system, Keller and Hongo found that short residence time was more responsible for low levels of nitrous oxides in

\[ O + N_2 \rightarrow NO + N \quad k = 1.9 \times 10^{14} \exp(-319,200 / RT) \]

\[ N + O_2 \rightarrow NO + O \quad k = 6.4 \times 10^9 \exp(-26,288 / RT) \]

\[ N + OH \rightarrow NO + H \quad k = 3.8 \times 10^{13} \]

\[ C_{NO} = 4.6 \sqrt{C_o C_n} e^{\left(\frac{-10860}{T}\right)} \]

Equation 3.2 The Zeldovich NO production mechanism. \( k \) is the specific reaction rate constant, \( R \) is the universal gas constant, and \( T \) is temperature. Keller and Hongo disregarded all but the first reaction in their analysis [71].

Equation 3.3 The Zeldovich correlation [19]. Severyanin cited the Zeldovich correlation as being capable of predicting nitrous oxide concentration in exhaust gas from pulsating burners [19]. Keller and Hongo also used the Zeldovich NO formation mechanism for their calculations [71].
the exhaust gasses from the pulsating combustor than was lower combustion temperatures [71]. The authors concluded that lower temperatures (generally attributed to so-called automatic exhaust gas recirculation), however, still played a critical role.

### 3.8.7 Case Studies: Drying Involving Pulsating Combustors

In 1994, Brandt, et al., treated coalbed brine using a three-part approach [68]. They started by concentrating the brine using reverse osmosis, followed by evaporation via a submerged heater, and finishing with spray drying using a pulsating combustor. The initial brine feed was 1,000 m$^3$/d (183.5 gpm) at 7,000 ppm TDS, which reverse osmosis concentrated to 26,800 ppm (retentate) at a rate of 250 m$^3$/d (45.9 gpm). Using a submerged heater, brine solvent was evaporated, reducing the waste stream to 25 m$^3$/d (4.6 gpm) but increasing the TDS concentration to 268,000 ppm. This solution with suspended salt precipitate was shipped to a facility where a dryer that used a pulsating combustor was applied for solvent evaporation. Brant, et al., reported that this convective drying step yielded an end product of “a very fine-grained dry powdery salt with excellent appearance” and a 3% moisture content. According to the authors, the evaporative power usage of the dryer that employed a pulsating combustor was 2.65-2.75 MJ/kg.

A 2002 study performed by Wu and Liu investigated the atomization and drying properties of a spray drying system that used a pulsating combustor, as shown in Figure 3.13 [69]. They fed a 10% (kg/kg) NaCl solution at 27°C (81°F) and 0.0057 kg/s (about 0.1 gpm) into the tailpipe, 1.5 m (4.9’) from the combustion chamber. The brine was introduced using a 14 mm (0.55”) inner diameter pipe. Using liquefied petroleum gas as fuel, the pulsating combustor had a 25 kW heat load and resonated at 83 Hz. Wu and Liu found the system used 3.3 MJ per
kilogram of water evaporated.

Further, using an optical analyzer, the authors found that droplet diameter was very uniform (averaging 44.01 μm), and about half as small as droplet diameters reported for conventional nozzle-dependent spray dryers. They also found that, on the basis of volumetric comparison of drying chambers, their pulsating combustion spray dryer had a volumetric evaporation rate more than six times greater than that of conventional spray drying (217 kg/m³·hr versus 30 kg/m³·hr). Wu and Liu also noted that droplet diameter was crucial to drying rate.

In a 2014 paper, Wu, et al., reported on drying an egg white solution (13.04% solids) using a Pulse Combustion Systems™ (Payson, AZ) pilot-scale drying system [10]. Solution feed rate was 0.6 kg/min (about 0.16 gpm), and the system reduced moisture content from 86.96% to 8.11% percent with a 33.62 kg/hr (74 lb/hr) water evaporation rate. The fuel source for the pulsating combustor was propane, which was fed at 0.63 m³/min, and the desired combustor
power was 24.32 kW. For this system, exhaust gas temperature was controllable, and the system was pre-warmed for 30 minutes. Reported energy usage was 2.604 MJ/kg.\textsuperscript{26} Wu, \textit{et al.}, found that 26.48\% of the feed solids was not recovered, and speculated that it may have been lost in the baghouse.

### 3.8.8 Caveats

Presently, pulsating combustors have a limited niche in industrial drying [6]. Properly designed units are recognized as safe and reliable. Yet pulsating combustors are not commonplace. They remain novelties [8]. Although the noise they generate is often cited as perhaps the primary reason for their limited industrial use, there are other issues that may make the use of pulsating combustors in practical applications challenging.

In 1986, Putnam, \textit{et al.}, claimed that mechanically-valved pulsating combustors could be readily designed for specific applications, based on an amassed empirical knowledge base [1]. Although this statement indicates that the design of a pulsating combustor for a practical purpose is possible, Putnam, \textit{et al.}, go on to explain that, when it comes to designing pulsating combustors, the “wheel has been re-invented many times.” They attribute this to a lack of communication between researchers and large amounts of unpublished data on the topic of pulsating combustion. More than three decades later, little appears to have changed. The design of pulsating combustors still relies on trial and error, and scaling from pilot to industrial sized units remains an unsolved problem [3, 5-7, 13, 21, 51]. Kudra perhaps said it best, “Even though pulse-combustion dryers [have been] in the market for years, the design and operation of pulse-combustion dryers still belongs to art rather than science, mostly because of complex

\textsuperscript{26} The authors, however, provide the latent heat of vaporization for water as 2.258 MJ/kg.
phenomena involved in pulse combustion and interaction of the sonic waves with the drying chamber and the drying material” [21]. This lack of fundamental knowledge often leads to suboptimal design, high research and development costs, and tiresome, tedious experiments [8, 9].

Another open issue is that it is possible to create a functioning pulsating combustor, but it may operate in a sub-optimal manner [3]. Zbicinski, et al., defined optimal performance as being, “[I]f the combustor produces smooth and high amplitude pressure oscillations of low content of toxic substances in the flue gases” [65]. Figure 3.14 visually shows via time versus pressure oscillation graphs the difference between optimal and non or sub-optimal pulsating combustion conditions. Though the specifics of the combustor type and level of operator control over the system are unclear based on the source’s description, it is clear that the combustion chamber volume was deliberately changed by 600 cm³ [65]. The purpose of these figures is to demonstrate how changes to the pulsating combustor can alter (and possibly degrade) its performance. Because the complexities and unknowns of rapidly varying pressure, temperature, and velocity profiles and regions in pulsating combustion concern over proper unit design seems common [44].
Figure 3.14 Combustion chamber pressure oscillations. There are several noted changes between both conditions; not noted is that in condition (a) the volume of the combustor chamber is 1,000 cm$^3$; whereas in (b) it is 400 cm$^3$ [65]. According to the source, the primary purpose in comparing and contrasting these plots is to show the “non-optimal point of combustor performance” (a) versus the “optimal point of combustor performance.” Because a the combustor had a “conical-cylindrical combustion chamber” and the combustor tailpipe length is identical for each condition shown, it is possible that this was a pulse combustor, where combustion frequency and air and fuel flow rate were uncontrollable, and the difference in body geometry between the two conditions shown is primarily responsible for all the observed differences – most notably the shape and amplitude of the pressure oscillations.
3.8.9 Current State of Research

Presently research on the topic of pulsating combustion predominantly focuses on computer modeling. There are several key reasons for this. First, being able to predict pulsating combustion behavior would avoid tedious empirical system development [73]. Second, the physical conditions within pulsating combustion systems are usually too harsh and too transient for reliable, detailed, and accurate measurements, which are necessary for accurate calculations (e.g., instantaneous spatial pressure, temperature, and velocity measurements, etc.) [59]. Consequently, developing a successful computer model would greatly advance the collective understanding of pulsating combustion technology and encourage its widespread use.

For the same reasons that computer models of pulsating combustion are necessary, creating accurate models may be prohibitively difficult. This is because steady or quasi-steady equations and theories (which are commonly used and well-understood) cannot explain the behavior of a pulsating combustor [51]. While computer programs can be used to model turbulent gas dynamic (and hydrodynamic) interactions with small pressure gradients, most software lacks the capability to model a full-scale pulsating combustor [15]. Thus, most modern research on the topic of pulsating combustors occurs in the computer science and mathematical fields, as scientists and engineers pursue an accurate, fully-functional model of the pulsating combustion phenomenon.
3.9 Summary

Although employed in limited use, spray dryers that use pulsating combustors are effective. In 2002, Kuts, et al., reported a resurgence of interest in the application of pulsing combustors as industrial dryers [15]. Strumillo, et al., call spray drying via a pulsating combustor, “[O]ne of the most promising methods of disperse drying” [44]. As discussed, the intensity and efficiency of combustion achieved within pulsing combustors exceeds that which conventional combustors can achieve [47]. This translates into enhanced convective heat transfer, which reduces energy drying costs. Thus the technology of pulsating combustion can overcome the leading limitation of conventional spray drying.
3.10 References


CHAPTER 4: THESIS OBJECTIVES

4.1 Project Introduction

The research upon which this thesis is based was set into motion when Furness-Newburge, Inc. constructed their super-charged pulsed jet combustor. The author’s primary academic adviser (Dr. Fred S. Cannon) and Furness-Newburge have a long history of jointly developing innovative solutions to industrial, environmental compliance problems. The initial purpose of the super-charged pulsed jet combustor was to dehydrate bentonite-clay slurries, for bentonite reuse in metalcasting foundries. At the suggestion of Dr. Cannon, and with the assistance of Thomas Geeza, initial proof-of-concept salt-water-separation experiments were conducted at Furness-Newburge’s Versailles, KY facility.

The initial, driving hypothesis of this research was that some mechanism or force unique to the exhaust region of this proprietary super-charged pulsed jet combustor could separate dissolved solids from water, using less energy than required by conventional thermal desalination systems. Furthermore, this affect was said to be uninfluenced by the salinity or chemistry of the solution introduced into it. Thus this system presented a major breakthrough in the field of desalination.

A significant funding source for this project was the National Science Foundation, via an EArly-concepts Grant for Exploratory Research (EAGER). This grant was ideal for this project, because the primary purpose of the EAGER funds is enabling high-risk exploratory work that has the potential to be revolutionary [1]. Another funding source was the Ben Franklin

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27 The author of this thesis was also funded by two National Science Foundation Research Experience for Veterans grants.
Technology Program, with co-funding from Hydro Recovery, LP. These funds enabled the super-charged pulsed jet combustor to come to Penn State University for exploratory research and evaluation – the results of which are presented in the following three chapters of this thesis.

4.2 Thesis Objectives

The objective of this project was to demonstrate that the super-charged pulsed jet combustor built by Furness-Newburge was capable of treating highly complex wastewater from the natural gas industry. As discussed in Chapters 1 and 2, petroleum production industries need cost-effective solutions for treating their hypersaline wastewater. Chapter 3 made the case that a system that may be similar to spray drying coupled with a pulsating combustor may present a possible solution. With few exceptions, there does not appear to be any previous or current work on using such a system to remediate wastewater produced by the fossil fuel production industries. Thus the system presented herein is both necessary and novel.

The research in this thesis is unconventional. A very detailed and thorough investigation of the super-charged pulsed jet combustor and its supporting hardware required advanced knowledge in the fields of mechanical, chemical, acoustical, and aerospace engineering. Because of this, the research conducted by the Penn State University Environmental Engineering team took an independent, investigative, and unconventional approach.

4.3 Thesis Format

This thesis is composed of seven chapters and three appendices. Chapter 1 is a detailed introduction to hydraulic fracturing – the process itself, and the economic and environmental issues surrounding the practice. Chapter 2 explores the origin, composition, and fate of wastewater produced by hydraulic fracturing. This chapter is important because it demonstrates
the need for a unique salt-water separation process specifically for hypersaline, hydraulic fracturing wastewater. Chapter 3 provides a literature review of conventional technologies which may be related to the system presented in this thesis. This chapter, Chapter 4, is a focus and transition point, which introduces the research conducted by the author on hypersaline brine remediation.

The research conducted with the super-charged pulsed jet combustor at Penn State University is presented in reverse chronological order in Chapters 5 through 7. Chapter 5 presents the most current findings regarding the performance of the system when processing hypersaline saline brines. The chapter begins with a brief introduction, a discussion of materials and methods, a presentation of the results, and a discussion thereof. Chapter 6 retro-actively discusses some of the details of some of the system characterization experiments initially conducted with the system at Penn State University. Chapter 7 details the initial experiments performed with the system at Penn State.

Chapter 8 serves as a project summary, and points toward areas requiring further, future investigation.

Regarding the three appendices to this thesis: The first, Appendix A, covers work done to remove radium from natural gas wastewater via co-precipitation. The author worked collectively with three other Penn State researchers (Cesar Nieto Delgado, María I. Zermeño Montante, and Mat Brener) on this topic.

Appendix B is a brief discussion of the power provided to the super-charged pulsed jet combustor system via compressed air. It predominantly supports research done in Chapter 6. Due to its tangential nature, however, it was not included in the main body of the thesis.
Appendix C covers a large body of work which the author performed on developing and characterizing an environmentally-friendly, core sand binder for the ferrous metal casting industry. Under the guidance of Dr. Fred Cannon, Dr. Bob Voigt, and Dr. John Fox, the author originally began his studies on this project. This endeavor, however, was cut short by the author’s deployment to Afghanistan with the Pennsylvania Army National Guard in support of Operation Enduring Freedom. The author returned to Penn State, but began working on the super-charged pulsed jet combustor project along with Mr. Thomas Geeza and Dr. Cannon.
4.4 References

2014].
CHAPTER 5: TESTING AND EVALUATING THE PROCESS

5.1 Introduction

The research related in this chapter sought to demonstrate that the super-charged pulsed jet combustor is a viable hypersaline brine remediation technology. With the modifications and experimental setup described herein, the system was sufficient to demonstrate this at the proof-of-concept level.

5.2 Materials

5.2.1 The Combustor

The body of the super-charged pulsed jet combustor is comprised of four cylindrical sections made from stainless steel. Each section is joined to the other using a wrap-around clamp. Overall length is 2.9’ (0.9 m). All sections have a 5” (12.7 cm) outer diameter, and the internal bore diameter of the central tailpipe piece is 2.6” (6.6 cm). A spark plug ignited the fuel-air mixture inside the combustion chamber; the current for which was generated by a magneto.

5.2.2 Fuel

Propane fueled the super-charged pulsed jet combustor. Propane is a common fuel for pulsating combustors [1-4]. Based on literature, the expected composition of the commercial-grade propane used in this research is 97.3% C₃H₈, 2.2% C₂H₆, and 0.5% C₄H₁₀ [5].

Propane flowed from a compressed cylinder to an air-fuel mixing chamber from which it went into the combustion chamber. An operator visually measured the flow of gaseous propane using an acrylic flowmeter. The propane flow rate was manually adjusted by the operator using
a needle valve. The operator used a pressure regulator set the fuel pressure to 40 psi (275.8 kPa) for all experiments discussed in this chapter.\textsuperscript{28} Fuel mass flow rate was recorded by measuring the mass decrease of the propane tank.

5.2.3 Air

Preceding the air-fuel mixing chamber, an externally-controlled, mechanically-actuated rotating valve allowed compressed air to be injected into the combustion chamber in pulses. An electric motor spun the valve. By regulating the voltage applied to the DC motor, the operator controlled air valve speed (which was determined using a proximity sensor). By regulating the air injection frequency, the frequency of pulses of combustion were regulated. Air flow rate was measured using an acrylic flow meter, and the pressure of the flow was regulated using a ball valve.

5.2.4 Fluid

During all the experiments related in this chapter, an artificial surrogate hypersaline brine solution was used. It was created in five gallon (18.9 L) batches by mixing tap water and commercial water softening NaCl pellets in a stirred, heated (100\textdegree C) bath. The total dissolved solids (TDS) concentration of the surrogate brines was experimentally determined. The average TDS concentrations for the two salt brines used during these experiments was 141,000 mg/L (13.1\% salt by mass) and 278,000 mg/L (24.2\% salt by mass).

\textsuperscript{28} All pressures reported in this thesis refer to gauge, not absolute pressures, unless otherwise noted.
5.2.5 Pumps

Two diaphragm chemical metering pumps were used for fluid delivery. Pump flow was manually adjusted by setting stroke length and/or frequency.

5.2.6 Liquid Flow Measurement

A bucket of brine was placed atop an electronic scale. Brine was pumped from the bucket through the system. The scale was digitally connected to a computer, enabling fluid mass flow through the system to be recorded throughout the experiment.

5.2.7 Heat Exchanger

Two equally-long pieces of 3/8” (0.9525 cm) outer diameter stainless steel tubing were wound around the outside of the body of the super-charged pulsed jet combustor. Where they joined, a wetted pressure gauge was installed. The heat exchanger coils around the pulsed combustor body were liberally wrapped in ½” thick (1.27 cm) insulation. As shown in Figure 5.1, fluid flowed through the tubes, going from the exhaust end of the combustor to its combustion chamber region.

Figure 5.1 An example of the fluid heat exchanger around the combustor body, showing the flow direction of the fluid, and the exhaust from the combustor. Drawing is not to scale. View is from directly above the combustor, which is shown sitting on its stand.
5.2.8 Thermocouples

Five ungrounded, ¼” (0.64) outer diameter thermocouples were used to monitor system temperatures. One thermocouple measured initial brine temperature. One measured brine temperature after the heat exchanger around the combustor body, but prior to the injection of the brine into the combustor’s exhaust. Three thermocouples measured the outer skin temperature of the combustor body along its length.

5.2.9 Data Acquisition & Software

A data acquisition unit transmitted electronic signals between the electrical devices of the system and a computer equipped with LabVIEW software. System data was collected every second from all connected electronic devices.
5.3 Experimental Methods

5.3.1 Determining the Concentration of Solids within Liquids

The author experimentally developed a method to dehydrate hypersaline brine samples without splattering. Five to 10 mL of fluid were collected and poured into clean pre-weighed crucibles. A measured volume of liquid brine was poured into the crucible, and their combined weight was recorded. The liquid-filled crucibles were dried at 90°C (194°F) in an oven overnight. For the final hour which the crucibles were in the oven, the temperature was raised to 220°C (>428°F) to remove liquid water molecules which may have been trapped within the salt crystalline structure. This protocol avoided partially moist or splattered samples that have been reported when conducting similar solids-concentration-in-liquid analysis on similar hypersaline brines [6].

Once the water had evaporated, the crucibles were allowed to cool for one hour and then were reweighed. Dividing the dried mass increase of the crucible by the volume of brine initially added to it yielded the solids concentration of the liquid brine (reported herein as “total dissolved solids” or “TDS”).
5.3.3 Process Procedure

For each test, the combustor was pre-warmed. Once brine temperatures throughout the system were stable, the brine was injected into the exhaust from the super-charged pulsed jet combustor. Brine injection into the exhaust lasted for 10 minutes (600 s) on average.

To introduce the brine into the exhaust of the super-charged pulsed combustor, a ½” (1.27 cm) diameter injector was fabricated. As shown in Figure 5.3, it was given a “U” or “goose-neck” shape. This injector directed the brine flow vertically down into the exhaust gas stream. It was fabricated so that it ended ¼” (0.64 cm) above the top edge of the combustor body.

While brine was injected into the exhaust gas, a thin-walled round plastic basin collected whatever solid or liquid mass fell to the ground, under the influence of gravity, within about five feet (1.5 m) from the end of the combustor. This plastic basin collected a high percentage of effluent mass from the process (because most non-gaseous particles had a downward

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29 The author called it a “down spout.”
momentum in an area covered by the pool) making it an effective control volume.

At the conclusion of each experiment, the mass within the plastic basin was physically segregated by its predominant phase (i.e., mostly liquid or mostly solid) as shown in Figure 5.4. The mostly liquid mass was collected into a pre-weighed bucket, from which samples for solids-in-water (i.e., TDS) analysis were immediately taken. Having been weighed prior to the experiment, the emptied plastic basin was re-weighed. Its increase in mass represented the mostly solid fraction of collected mass. Based on the initial concentration of the brine used in the experiment, a fixed percentage for the solids to liquids ratio of the mostly solid mass fraction was used to further characterize the collected mass.

By this extensive mass fractioning process, a mass balance of water and salt could be calculated across the system, from which various subsequent analyses could be conducted.

**Figure 5.4 The mass fractioning and mass determination process.** Mass collected in the plastic basin is physically segregated and categorized as being either mostly liquid or mostly solid. It is subsequently divided into completely solid and liquid mass amounts, by the methods shown.
5.4 Results Regarding Salt-Water Separation

Over the course of seven days, thirteen tests were conducted. Employing an open-air system, these tests appraised the extent to which the super-charged pulsed jet combustor could vaporize water from a hypersaline brine, and subsequently collect salt in a plastic basin.

For these experiments brine concentration and flow rate were deliberately varied. In all experiments air and fuel flow to the combustor were kept constant. The down spout or “goose-neck” injector was also used in all these experiments.

As shown in Table 5.1, for the thirteen experiments conducted two brine concentrations were used. For the first seven experiments, the average solids concentration of the feed brine was 278,346 mg/L (24.2% solid salt, by mass). Brine flow through the system averaged 0.0285 kg/s (0.39 gpm). These were followed by six experiments conducted using a brine with an average dissolved salt concentration of 141,095 mg/L (13.1% solid salt, by mass). With the lower salt concentration, the average brine flow was 0.0186 kg/s (0.28 gpm).
Table 5.1 The thirteen tests conducted to determine the super-charged pulsed jet combustor's salt-water separation properties at different salinities and brine flow rates.

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<th>Brine Flow (gpm)</th>
<th>Experiment Time (s)</th>
<th>Brine Mass Processed (kg)</th>
<th>Feed TDS (mg/L)</th>
<th>Density (mg/L)</th>
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</table>

| x          | 278,346 | 3,377      | 1.1566   0.0077 |
| σ          | 2,532   | 1,816      | 0.0048   0.0011 |

| x          | 141,095 | 1,588      | 1.0718   0.0088 |
| σ          | 4,609   | 580        | 0.0045   0.0023 |
Fluid mass flow rates were determined by graphing the automatically recorded mass measurements from the electronic scale upon which the brine source bucket sat. Finding the linear slope of the line ($R^2$ always $\geq 0.99$) yielded average brine mass flow rate in units of kilograms per second (kg/s). Because the density of the feed brine was experimentally determined, the volumetric fluid flow in gallons per minute (gpm) could be calculated. The total mass processed through the system during an experiment was then calculated by multiplying the fluid mass flow rate by test time.

As described in the Methods section (Section 5.3) solid (i.e., salt) and liquid (i.e., water) mass fractions were tracked across the system. This is shown in Table 5.2 on the following page. For the mostly liquid fraction of collected mass, once the solids concentration of the solution was experimentally determined (i.e., TDS), the mass of solids in the brine could be determined by multiplying the mass of the brine ($m_{\text{solution}}$) by the TDS concentration, divided by the measured density of the brine. As shown in Equation 5.1, this yielded the mass of solids in the brine ($m_{\text{solids}}$). Because the brine was an artificial surrogate, it contained only salt and water. Therefore, the mass of water ($m_{\text{water}}$) in the brine was determined by subtracting the mass of the solids in the brine from the total mass of the brine.

\[
m_{\text{solids}} = m_{\text{solution}} \times TDS_{\text{solution}} \times \rho_{\text{solution}}^{-1}
\]

\[
m_{\text{water}} = m_{\text{solution}} - m_{\text{solids}}
\]

Equation 5.1 The equations used to determine solid (i.e., salt) and liquid (i.e., water) masses, where $m$ represents mass, TDS stands for total dissolved solids, and $\rho$ represents brine density.
Table 5.2 Solid (i.e., salt) and liquid water masses across the process.

<table>
<thead>
<tr>
<th>Date</th>
<th>Test #</th>
<th>Brine Flow (kg/s)</th>
<th>Brine Flow (gpm)</th>
<th>Water Flow (kg/s)</th>
<th>Water Flow (gpm)</th>
<th>% Salt, average (brine)</th>
<th>Mass Processed through System (kg)</th>
<th>Mostly Liquid</th>
<th>Mostly Solid</th>
<th>Total</th>
<th>Percent of Total Collected</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total</td>
<td>Solids</td>
<td>Water</td>
<td>Solid</td>
<td>Water</td>
</tr>
<tr>
<td>8/26/2014</td>
<td>1</td>
<td>0.025</td>
<td>0.34</td>
<td>0.019</td>
<td>0.30</td>
<td>14.19</td>
<td>3.41</td>
<td>10.78</td>
<td>2.30</td>
<td>5.30</td>
<td>0.480</td>
</tr>
<tr>
<td>8/28/2014</td>
<td>1</td>
<td>0.030</td>
<td>0.42</td>
<td>0.023</td>
<td>0.37</td>
<td>16.36</td>
<td>3.90</td>
<td>12.46</td>
<td>2.84</td>
<td>6.59</td>
<td>0.420</td>
</tr>
<tr>
<td>9/4/2014</td>
<td>2</td>
<td>0.026</td>
<td>0.35</td>
<td>0.020</td>
<td>0.31</td>
<td>10.40</td>
<td>2.50</td>
<td>7.89</td>
<td>1.67</td>
<td>3.47</td>
<td>0.486</td>
</tr>
<tr>
<td>9/9/2014</td>
<td>1</td>
<td>0.035</td>
<td>0.48</td>
<td>0.027</td>
<td>0.42</td>
<td>21.03</td>
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<td>15.94</td>
<td>4.96</td>
<td>11.88</td>
<td>0.132</td>
</tr>
<tr>
<td>9/15/2014</td>
<td>2</td>
<td>0.033</td>
<td>0.45</td>
<td>0.025</td>
<td>0.39</td>
<td>27.30</td>
<td>6.56</td>
<td>20.74</td>
<td>6.00</td>
<td>15.16</td>
<td>0.141</td>
</tr>
<tr>
<td>9/23/2014</td>
<td>3</td>
<td>0.021</td>
<td>0.31</td>
<td>0.018</td>
<td>0.29</td>
<td>12.60</td>
<td>1.67</td>
<td>10.93</td>
<td>1.33</td>
<td>5.32</td>
<td>0.124</td>
</tr>
<tr>
<td>9/25/2014</td>
<td>2</td>
<td>0.017</td>
<td>0.24</td>
<td>0.014</td>
<td>0.23</td>
<td>9.90</td>
<td>1.33</td>
<td>8.57</td>
<td>0.99</td>
<td>3.53</td>
<td>0.121</td>
</tr>
<tr>
<td>9/25/2014</td>
<td>3</td>
<td>0.016</td>
<td>0.24</td>
<td>0.014</td>
<td>0.22</td>
<td>9.42</td>
<td>1.27</td>
<td>8.15</td>
<td>0.91</td>
<td>2.96</td>
<td>0.109</td>
</tr>
</tbody>
</table>

130
During the experiments conducted using the 13.1% (salt by mass) brine, the residual mass which remained in the plastic basin, following physical segregation of the collected mass, appeared to be entirely solid salt. This conclusion was made because, once the mostly liquid collected mass had been poured out of the basin into a tared bucket, the team observed the mass remaining in the basin to be almost exclusively a crystalline precipitate covering the walls of the plastic basin.

For the tests which employed the brine with an initial concentration of 24.2% (salt by mass) brine, the team observed a low-viscosity hydrated salt paste that was frequently left behind in the plastic basin following physical mass segregation. In future experiments, the team will use thermal dehydration to experimentally determine the precise solid-to-liquid ratio of this paste for each experiment wherein it occurs. For the results presented herein, however, the residual mostly solid mass in the plastic basin, for experiments conducted using an initial brine strength of 24.2% (salt by mass) was assumed to be 60% solid salt, by mass.
5.5 Discussion

5.5.1 Vaporization of Water

As the mass flow rate of brine through the system increased, the percentage of water mass (as a percentage of the total water mass processed through the system during an experiment) collected in the plastic basin increased.\(^{30}\) This collected liquid water mass was not vaporized. Figure 5.5 shows this upward trend, which appears to apply for both experiments with high and low brine concentrations. By including water vaporization data gathered during experiments that used the same experimental system setup as shown herein, it was also found that the vaporization results closely matched those found when processing the brines.\(^{31}\)

As shown in Figure 5.6, in the range of 0.17-0.48 gpm (0.011-0.03 kg/s) water flow rates, the brine and tap water data plotted on the same graph show good trend correlation and show good correlation to a linear trendline fit. For example, both linear trendlines have roughly equivalent slopes.

For the experiments with a water flow rate range of 0.018-0.020 kg/s (0.29-0.31 gpm), the average amount of energy required to vaporize a kilogram of solvent water was 6.4 MJ/kg. The lowest energy requirement was 5.6 MJ/kg.

\(^{30}\) To compare brine data results with tap water results, the flow rate through the system is given herein as the flow rate of water through the system.

\(^{31}\) To accurately compare the results for the tests with the 24.2% (by weight) and 13.1% (by weight) brines to those with tap water, all flow rates were calculated to put them in terms of water flow rate (not brine) through the system.
Figure 5.5 The mass of water collected in the pool as a percentage of the total water mass processed through the system for brine and tap water tests.
Figure 5.6 Linear trendline fits for the experimental data in the flow range between the 0.17-0.48 gpm (0.011-0.03 kg/s) range of water flow rates through the system. Solid line is the linear trendline fit for the brine data. Dashed line is the linear trendline fit for the tap water data.
5.5.2 Salt Collection

The amount of salt collected in the plastic basin was discerned using the method presented in Section 5.4, and the results are presented in Figure 5.7. As much as 99% of the salt which was process through the system was collected in the plastic basin.

This collection highlights the favorability of this super-charged pulsed jet combustor for separating dissolved salts and solvent water. These results indicate that this system can keep nearly all the formerly dissolved or suspended salt with the collected un-vaporized liquid water. The team perceived that the mistified fluid acts as a scrubber or demister, recapturing salt particles that were mobilized in the air phase. These demisters are commonly used in single effect evaporation systems to control particulate matter emissions [7]. Therefore, little particulate material would have to be removed in a full-scale, closed-system reproduction of this system. The team aims to capitalize on the novel scrubbing phenomena observed in subsequent operations.
Figure 5.7 The mass of salt collected in the plastic basin after each experiment, reported as a percentage of the total salt that was in the brine.
5.5.3 Effect of outdoor ambient temperature and humidity

When operating in open-air mode, as herein, relative humidity and temperature may affect the performance of the super-charged pulsed jet combustor system. For a given ambient outdoor air temperature and barometric pressure, there is a limited water-vapor capacity of the air ($x_s$), as shown in Equation 5.2. This is the maximum theoretical mass of water vapor (reported in grams) which can be held in a mass of air (1 kilogram).

Relative humidity is a measure of the water content of the air for a given temperature, reported as a percentage (e.g., “50% relative humidity”). Thus, for this discussion, if the relative outdoor humidity on a particular day is said to be 50%, then half of the maximum theoretical water vapor capacity of the air ($i.e., x_s$) is already filled with water molecules [8]. Therefore, only 50% of the maximum theoretical water vapor capacity of the air may be available to hold water molecules vaporized into it. Thus the vapor capacity of the ambient outdoor air may be limited. This capacity limitation could possibly affect the vaporization performance of the open-air super-charged pulsed jet combustor, described herein.

To discern whether or not the maximum theoretical water vapor capacity of the air and the relative humidity on the particular testing dates had any perceivable effect on the vaporization performance of the system, the following analysis was performed. First, the

\begin{equation}
    x_s = \frac{0.62198 p_{ws}}{p_a - p_{ws}}
\end{equation}

*Equation 5.2* The maximum theoretical mass of water vapor which can be held in air at a given temperature is the specific humidity ratio at saturation ($x_s$). $p_{ws}$ is the saturation pressure of water (which depends on temperature, which is known by meteorological data), and $p_a$ is atmospheric pressure (which is provided by meteorological data).
atmospheric conditions for each day at noon were found using historic, meteorological data.\textsuperscript{32} Using standard values for the saturation pressure of water at the average daily temperature, the maximum theoretical water vapor capacity of the air ($x_s$ in units of grams of water per kg of air air) could be found for each day. These values are shown in Table 5.3.

The maximum theoretical water vapor capacity of the air was then reduced by the relative humidity to reflect the remaining water vapor capacity of the air ($x_c$). This step is shown in Equation 5.3, and the values for $x_c$ are shown in Table 5.3.

In addition to perhaps being affected by ambient conditions, the mass of solvent water vaporized by the open-air super-charged pulsed jet combustor was also directly dependent on the flow rate of brine (which can be corrected to the flow rate of water) through the system. To account for the direct influence of water flow rate through the system on the percent of water vaporized, the percentage of water mass not collected in the pool (\textit{i.e.}, vaporized) was multiplied by the water flow rate through the system. These values are shown in the rightmost column of Table 5.3.

\begin{equation}
x_c = x_s \times \frac{100 - RH}{100}
\end{equation}

\textbf{Equation 5.3} The remaining water vapor capacity of the ambient air ($x_c$), where $RH$ is the relative humidity and $x_s$ is the maximum theoretical water vapor capacity of the air based on ambient meteorological conditions.

\textsuperscript{32} Noontime was selected because experiments were routinely conducted over the noon hour on each testing date.
Table 5.3 Detailed outdoor ambient and humidity capacity results for each test date, yielding $x_s$ and $x_c$. Also included is the average percent of water vaporized corrected for its relationship to water flow rate through the system.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>$T$ (°C)</th>
<th>Relative Humidity (%)</th>
<th>Barometric Pressure (kPa)</th>
<th>$x_s$ (g$<em>{water}$/kg$</em>{air}$)</th>
<th>$x_c$ (g$<em>{water}$/kg$</em>{air}$)</th>
<th>Water flow x percent of water vaporized (kg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/26/2014</td>
<td>12:53 PM</td>
<td>24</td>
<td>53.0</td>
<td>30.22</td>
<td>102.34</td>
<td>18.70</td>
<td>8.79</td>
</tr>
<tr>
<td>8/28/2014</td>
<td>12:53 PM</td>
<td>21</td>
<td>53.0</td>
<td>30.07</td>
<td>101.83</td>
<td>15.61</td>
<td>7.34</td>
</tr>
<tr>
<td>9/4/2014</td>
<td>12:10 PM</td>
<td>24</td>
<td>78.0</td>
<td>30.17</td>
<td>102.17</td>
<td>18.73</td>
<td>4.12</td>
</tr>
<tr>
<td>9/9/2014</td>
<td>12:53 PM</td>
<td>17</td>
<td>82.0</td>
<td>30.22</td>
<td>102.34</td>
<td>11.98</td>
<td>2.16</td>
</tr>
<tr>
<td>9/15/2014</td>
<td>12:53 PM</td>
<td>17</td>
<td>59.0</td>
<td>30.22</td>
<td>102.34</td>
<td>11.98</td>
<td>4.91</td>
</tr>
<tr>
<td>9/23/2014</td>
<td>12:53 PM</td>
<td>16</td>
<td>55.0</td>
<td>30.37</td>
<td>102.84</td>
<td>11.16</td>
<td>5.02</td>
</tr>
<tr>
<td>9/25/2014</td>
<td>12:53 PM</td>
<td>16</td>
<td>72.0</td>
<td>30.38</td>
<td>102.88</td>
<td>11.16</td>
<td>3.12</td>
</tr>
</tbody>
</table>

Figure 5.8 The raw data of meteorological conditions (i.e., ambient outdoor temperature and relative humidity) and the percent water vaporization results for each of the thirteen tests conducted over seven days. Based on the raw data no discernable relationship seems to exist.
On four of the seven days that these experiments were conducted, multiple vaporization tests were performed (i.e., August 4, 9, 23 and 25). Therefore, on these dates the average of the individual results was used as the overall value for that day.

Presented in Figure 5.9 is the graphical result of the remaining water vapor capacity of the ambient air versus the amount of solvent water vaporized (accounting for the influence of water flow rate through the system) for each of the seven days during which the 13 experiments were conducted. A linear trendline was added to determine if there exists any discernable direct linear relationship between the remaining water vapor capacity of the air and the amount of water vaporized for the day on which the experiment was conducted. As shown by the low $R^2$ value (0.35), no direct linear relationship has been found.

5.6 Chapter Summary

The experiments related in this chapter appraised the potential for this system to serve as a hypersaline brine remediation technique. The setup used herein was capable of processing hypersaline brines which were 13.1% and 24.2% dissolved solid salt by mass. Furthermore, most of the salt remained with the non-vaporized water that was collected into a plastic basin beneath the end of the combustor. These results indicate that an intensive air-scrubbing system downstream of the super-charged pulsed jet combustor would not be necessary to remove particulate matter from the air, as part of a fully-enclosed system.
Figure 5.9 The remaining water vapor capacity of air ($x_c$) versus the average percentage of water mass vaporized by the super-charged pulsed jet combustor, on the date of each experiment. The direct relationship between water flow rate through the system and the percentage of water vaporized is accounted for by multiplying the water mass flow rate through the system by the percentage of water mass vaporized by the system.
5.7 References


CHAPTER 6: THERMODYNAMIC SYSTEM ANALYSIS

6.1 Introduction

Traditionally, conventional pulsating combustors are used as either heaters or dryers [1]. The proprietary super-charged pulsed jet combustor system used in this research, however, serves in both roles. First, thermal energy from the combustor body conductively heats fluid within heat exchanger coils wrapped around the combustor. Second, exhaust gas from the combustor acts on the fluid injected into it.

This chapter details experiments conducted to determine the thermodynamic behavior of this super-charged pulsed jet combustor. This was done by conducting energy balances. In other words, fuel (potential energy) enters the system. It is burned (combusted), releasing energy. This energy may take several forms; however, thermal energy (heat) is predominantly considered herein. (For example, the energy from combustion which does not take the form of thermal energy exits the system as light, sound \([i.e., \text{pressure waves}], \text{etc.}\).)

In general, measuring thermal energy is relatively straight-forward, via temperature measurements. Some of the thermal energy resulting from the combustion of propane within the super-charged pulsed jet combustor goes to heating the combustor body. Some fraction of this thermal energy is conductively transferred from the skin of the body to the metal coils wrapped around it; and from these coils into the brine flowing through them. Some thermal energy exits the system by radiating into the surrounding air – either from the body or through the tailpipe.

By experimentally determining the fraction of the total input power that goes to each part of the system, the energy balance of the system can be determined.
6.2 Materials

In this thesis, the presentation of experimental results is given in reverse chronological order. Thus the description of the super-charged pulsed jet combustor and other system materials previously described in Chapter 5 is applicable to this chapter. The minor differences in system components unique to the research presented in this chapter are discussed in the Methods section of this chapter.

All experiments conducted during the research presented in this chapter used warm (≈ 30°C, 86°F) tap water from the Penn State University High Pressure Combustion Lab. Tap water was pushed through the system using one of two methods. One technique used a chemical metering pump. The second fluid delivery method directly used the High Pressure Combustion Lab’s tap water distribution system (i.e., water was piped directly from the laboratory’s tap to the system).

6.3 Methods

The focus of the work related in this chapter is determining the thermodynamics of the system in two key regions: the heat exchanger around the combustor body, and its exhaust gas. In general, thermal energy transfer in heat exchangers is well understood. Consequently, the team identified the combustor’s exhaust as the primary research focus for the experiments related in this chapter.

To investigate the thermodynamics of the exhaust from the super-charged pulsed jet combustor, the team developed two experimental methods based on fundamental thermodynamic principles.

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33 Water density at this temperature is 995.7 kg/m³ (62.2 lb/ft³).
6.3.1 Front-end-coil

Power recovery across the system was determined by evaluating the increase in water temperature. Two thermocouples were installed in the system’s fluid line: one prior the heat exchanger around the body, and one after. To evaluate conductive heat transfer in the exhaust gas region, the team fabricated a “front-end-coil” apparatus, as shown in Figures 6.2 and 6.3. This was made by winding ¼” (0.64 cm) outer diameter, stainless steel tubing around a pipe with a 2” (5.08 cm) outer diameter. Removing the pipe left behind a neatly-formed, symmetrical coil, which was roughly the same diameter as the internal bore of the super-charged pulsed jet combustor (see Chapter 5, Section 5.2.1). One thermocouple was placed before the coil and one after it, to record the difference in water temperature across the array. The coil was then placed directly in the path of the exhaust gas, about ½” (1.27 cm) from the exhaust end of the combustor. The coil was carefully oriented so that the exhaust gas passed directly through its center.
Figure 6.3 shows a process diagram of the front-end-coil experiment. First, tap water flowed from the laboratory past a thermocouple ($t_0$), into the heat exchanger around the body. Flow was kept as high as possible to prevent water vaporization within the heat exchanger.\textsuperscript{34} Coming from the heat exchanger, fluid proceeded past a second thermocouple ($t_1$) and into the front-end-coil array. Before entering the front-end-coil, the temperature of the fluid was again recorded ($t_2$). Once the fluid passed through the small coil, its final temperature was recorded ($t_3$), and it was ejected out of the tubing into a bucket several feet away from the combustor.

\textsuperscript{34} This flow was manually calibrated, without the combustor operating, prior to the experiment. The average of three measurements was used.
6.3.2 Down spout orientation

Although the front-end-coil experiments offered a means of determining conductive heat transfer in the exhaust gas, the fluid was protected within the coils, and not exposed to the exhaust gas and convective heat transfer. To address this limitation, another experimental method was devised: Fluid was alternately injected into and out of the super-charged pulsed jet combustor’s exhaust. In both cases, the un-vaporized liquid-phase water mass was collected. By maintaining constant water flow rates (via a chemical metering pump) and keeping all other operating conditions constant, the difference in collected water mass between the two down spout orientations elucidated the thermodynamic properties of the super-charged pulsed jet combustor’s exhaust.

It was for this experiment that the team originally created the “down spout” or “goose-neck” injector (which was subsequently used in Chapter 5). When installed just beyond the exhaust end of the combustor body, the end of this “U” shaped pipe directed water down toward the ground. As shown in Figure 6.4, the down spout had two orientations: (1) directly into the exhaust gas, or (2) at an 180° angle away from the exhaust gas. In both cases, a large 5’ (1.524 m) diameter by 1’ (0.305 m) deep plastic tub was placed on the ground beneath the down spout, as shown in Figure 6.5. (This is the same plastic basin used in the experiments related in Chapter 5.) This plastic basin acted as a control volume, and captured the water that was not vaporized.
Figure 6.4 Down spout positions relative to the combustor’s exhaust end. Not to scale. (a) Shows the down spout position when water was injected into the combustor’s exhaust. (b) Shows the down spout rotated 180° degrees, such that water is still ejected through the pipe end, but out of the combustor’s exhaust.

Figure 6.5 A top view of the general experimental set up, where water is ejected down into the combustor’s exhaust gas, and whatever is not vaporized is collected in the large plastic basin on the ground.
6.4 Results & Discussion

6.4.1 Front-End-Coil Tests

Raising the temperature of a flow of liquid water requires the application of energy over time (i.e., power). Power is the rate of doing work. It is measured in Joules (J) per second, or Watts (1 W = 1 J/s). Therefore, by determining the temperature increase (ΔT) of a liquid flow a measurement of power (Q) can be calculated. Equation 6.1 shows this relationship, and this equation is commonly used to calculate the power of a heat exchanger [2, 3].

\[ Q = \dot{m} \cdot c_p \cdot \Delta T \]

System thermodynamic characterization using the heat exchanger around the combustor body and front-end-coil array was conducted four times. During the first experiment, the average tap water mass flow rate through the system was experimentally measured to be 0.1614 kg/s (0.35 lb/s) which corresponds to 2.55 gpm (579 lph).\(^{35}\) The average tap water mass flow rate through the system for the three subsequent tests was 0.0938 kg/s (0.21 lb/s) which corresponds to 1.49 gpm.

The average mass flow rate of gaseous propane to the combustor for the four experiments was 1.30 g/s (0.17 lb/min). Compressed air flow rate was maintained at about 23 SCFM, as read by the operator on an acrylic flowmeter.

After starting the combustor, tap water was allowed to flow through the system, and temperature data was collected by the computer. The average experiment length was 28.5 minutes. With temperature data measurements being automatically collected and recorded every

\(^{35}\) Using a water density of 995.7 kg/m\(^3\) (62.2 lb/ft\(^3\)) at 30°C.
second, this yielded an average data set of 1,710 measurements. From this data set, for the first experiment, the final 2.5 minutes were selected for analysis, and for the remaining three tests the final 3 minutes were selected. At these times, the combustor body and fluid temperatures across the system were found to be at steady-state.

Table 6.1 shows the temperature differences (ΔT) across both the heat exchanger around the body of the pulsed combustor and the front-end-coil, calculated using the collected temperature data. Having been experimentally determined, the mass flow rate of the tap water through the system (m) is known for each test. For all calculations, the specific heat of water (c_p = 4.18 kJ/kg·K) was used. Thus, using Equation 6.1, the power recovery across each heat exchanger could be calculated; and these results are shown in Table 6.1.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Water Flow Rate (kg/s)</th>
<th>Water Flow Rate (gpm)</th>
<th>Propane Flow Rate (g/s)</th>
<th>ΔT across Heat Exchanger (K)</th>
<th>ΔT across Front End Coil (K)</th>
<th>PowerRecovered Across Heat Exchanger (kW)</th>
<th>PowerRecovered Across Front End Coil (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1614</td>
<td>2.57</td>
<td>1.26</td>
<td>40.0 ±0.1</td>
<td>4.7 ±0.2</td>
<td>27.0</td>
<td>3.2</td>
</tr>
<tr>
<td>1</td>
<td>0.0913</td>
<td>1.45</td>
<td>0.86</td>
<td>26.0 ±0.1</td>
<td>4.2 ±0.2</td>
<td>9.9</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>0.0957</td>
<td>1.52</td>
<td>1.90</td>
<td>37.6 ±0.1</td>
<td>8.1 ±0.1</td>
<td>15.0</td>
<td>3.2</td>
</tr>
<tr>
<td>3</td>
<td>0.0945</td>
<td>1.50</td>
<td>1.18</td>
<td>33.2 ±0.1</td>
<td>6.2 ±0.2</td>
<td>13.1</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Having calculated the power recovered by the increase in fluid temperature through both the heat exchanger around the combustor body and the front-end-coil array, the input power to the system should be determined. Although there are several sources of power to the super-charged pulsed jet combustor system, among these fuel is predominant.  

When discussing power input to a system in the context of a thermodynamic system analyses, commonly used terms are “lower,” “higher,” and “gross heating values” for the fuel used [4]. For this research, the lower heating value (LHV) of propane (2,044 kJ/mol; 46.9 kJ/g) was used to determine the power input to the system from the fuel flow [2]. This value is appropriate because the lower heating value does not include the energy that can be recovered by re-condensing the steam within the combustion exhaust. In systems which do recover the energy from steam re-condensation, the higher (HHV) or gross (GHV) heating value of propane should be used (2,219.85 kJ/mol; 50.3 kJ/g) [2].

Completely oxidizing one mole of propane requires five moles of oxygen. Because air is 23.16% O\textsubscript{2} by weight and 20.95% O\textsubscript{2} by volume, it is the primary oxygen source for combustion [5]. Not all the propane fed to the combustor, however, is fully oxidized. And although this system may perhaps be related to conventional pulsating combustors which are known to very efficiently oxidize their fuels, no system is perfectly efficient [6-8]. Because the incomplete combustion of propane yields 29% less energy per mole than complete combustion (see Equation 6.2) future analysis will be conducted to precisely determine the combustion efficiency of the super-charged pulsed jet combustor.

---

36 Because this system relies on compressed air to achieve a super-charged effect, compressed air also represents a system energy input. To streamline this chapter, however, the detailed discussion and calculations of the power required to compress the air necessary to operate this system have been included as Appendix B.

37 Using a molar mass of 44.1 g/mol and a density of 493.0 kg/m\textsuperscript{3}, each completely oxidized gram of propane releases 46.9 kJ of energy.
\[ \text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g}) \quad 2,044 \text{ kJ/mol} \]

\[ \text{C}_3\text{H}_8(\text{g}) + 4\text{O}_2(\text{g}) \rightarrow 2\text{CO}(\text{g}) + 4\text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) \quad 1,448 \text{ kJ/mol} \]

**Equation 6.2** Complete (top) and incomplete (bottom) combustion reactions of propane and corresponding energies, without energy recovery from steam condensation.

Sans combustion gas analysis, it should be considered that a certain mass flow rate of propane is fed to the combustor, and even if it is not completely oxidized, the energy can be considered to be “expended” or “lost.” The results of applying this perspective to the fuel fed to the super-charged pulsed jet combustor for these experiments are shown in Table 6.2. As shown by the total system power recovery efficiency values, the total system efficiency for the first test (which had a tap water flow rate 72% higher than the average flow rate of the subsequent three tests) is nearly two times higher than the average total system power recovery efficiency for the other three experiments.

**Table 6.2** Combustor power and total system power recovery (through conductive thermal energy transfer) results from the four front-end-coil tests.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Water Flow Rate (kg/s)</th>
<th>Water Flow Rate (gpm)</th>
<th>Propane Flow Rate (g/s)</th>
<th>Power Recovered Across Heat Exchanger (kW)</th>
<th>Power Recovered Across Front End Coil (kW)</th>
<th>Total Power Recovered (kW)</th>
<th>Combustor Power (kW)</th>
<th>Total System Power Recovery Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1614</td>
<td>2.57</td>
<td>1.26</td>
<td>27.0</td>
<td>3.2</td>
<td>30.2</td>
<td>59.09</td>
<td>51.1</td>
</tr>
<tr>
<td>1</td>
<td>0.0913</td>
<td>1.45</td>
<td>0.86</td>
<td>9.9</td>
<td>1.6</td>
<td>11.5</td>
<td>40.33</td>
<td>28.5</td>
</tr>
<tr>
<td>2</td>
<td>0.0957</td>
<td>1.52</td>
<td>1.90</td>
<td>15.0</td>
<td>3.2</td>
<td>18.2</td>
<td>89.11</td>
<td>20.4</td>
</tr>
<tr>
<td>3</td>
<td>0.0945</td>
<td>1.50</td>
<td>1.18</td>
<td>13.1</td>
<td>2.4</td>
<td>15.5</td>
<td>55.34</td>
<td>28.0</td>
</tr>
</tbody>
</table>
As previously discussed (see Equation 6.1), power recovery through a heat exchanger is a function of the fluid mass flow rate through the system. At some point, the fluid flow rate is so high that the difference in fluid temperature flowing through it approaches zero. At this point, the maximum power recovery is achieved. Based on the power recovery results for the heat exchanger around the combustor body and for the front-end-coil array, at a water flow > 2.5 gpm (0.16 kg/s) through this system, the percent power recovery will asymptotically approach some maximum limit. As the results in Figure 6.6 show, the front-end-coil appears to have reached this limit. This implies that a maximum raw power recovery via conductive transfer of the thermal energy in the exhaust is about 3 kW.

Figure 6.6 Power efficiency (as measured against total system power) of each energy-recovery section (i.e., heat exchanger and front-end-coil array). Note that the front-end-coil array does not recover more power, when the water flow through the system equals 0.16 kg/s (2.57 gpm) while the heat exchanger around the combustor body does.
6.4.2 Down Spout Orientation Tests

Nine tests were conducted using the down spout orientation experimental technique. These were conducted over three days. The deliberate variable between the nine experiments was down spout orientation. Three tests were run with fluid ejected into the exhaust region of the pulsed combustor, and are labeled as “in.” Six experiments ejected water outside of the exhaust gas stream, and are labeled as “out.”

The same chemical metering pump was used for all tests. The pump was pre-calibrated to provide about 0.01 kg/s (0.165 gpm; 37.5 lph). Similarly, air and propane pressures and flow rates were kept as constant as possible. The average fuel mass flow rate of gaseous propane to the super-charged pulsed jet combustor was 1.26 g/s (0.17 lb/min).

After preheating the combustor, tap water flowed through the system and was ejected out the down spout above the plastic basin (which acted as a control volume) for 14 minutes. The tap water mass flow rate during this time period was more precisely determined by measuring the decrease in mass of the fluid source bucket, from the start to the end of the experiment.

As shown in Table 6.3 and Figure 6.7, significantly less liquid water mass was collected in the pool while injecting water into the exhaust gas. When the tap water was injected into the exhaust, on average 15.83% of the total tap water mass processed through the system during those three experiments was collected as liquid water in the control volume. However, when the tap water was ejected out of the exhaust from the super-charged pulsed combustor, on average 30.52% of the initial liquid mass was captured in the plastic basin.
Table 6.3 Water temperature and mass balances for the directional down spout experiments. Influent refers to the water temperature prior to the heat exchanger around the body; while effluent refers to the water temperature after the body heat exchanger but before discharge through the down spout.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Test Number</th>
<th>Water Flow Rate (kg/s)</th>
<th>Water Flow Rate (gpm)</th>
<th>Fuel Flow Rate (g/s)</th>
<th>Influent Water Temperature (°C)</th>
<th>Effluent Water Temperature (°C)</th>
<th>Water Mass Processed (kg)</th>
<th>Water Mass Collected (kg)</th>
<th>Percent of total water mass collected</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>1</td>
<td>0.0107</td>
<td>0.17</td>
<td>1.20</td>
<td>28.7 ±0.1</td>
<td>93.4 ±0.6</td>
<td>8.98</td>
<td>1.50</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0100</td>
<td>0.16</td>
<td>1.47</td>
<td>29.8 ±0.2</td>
<td>94.8 ±0.6</td>
<td>8.48</td>
<td>1.05</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0096</td>
<td>0.15</td>
<td>1.23</td>
<td>25.4 ±0.1</td>
<td>93.6 ±0.7</td>
<td>8.10</td>
<td>1.50</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.0090</td>
<td>0.14</td>
<td>1.19</td>
<td>26.8 ±0.1</td>
<td>93.9 ±0.7</td>
<td>7.55</td>
<td>2.20</td>
<td>29.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0097</td>
<td>0.15</td>
<td>1.23</td>
<td>27.2 ±0.1</td>
<td>94.4 ±0.6</td>
<td>8.73</td>
<td>1.90</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.0096</td>
<td>0.15</td>
<td>1.14</td>
<td>26.9 ±0.1</td>
<td>93.5 ±0.7</td>
<td>8.08</td>
<td>3.09</td>
<td>38.2</td>
</tr>
<tr>
<td>Out</td>
<td>5</td>
<td>0.0094</td>
<td>0.15</td>
<td>1.49</td>
<td>26.8 ±0.1</td>
<td>94.1 ±0.9</td>
<td>7.75</td>
<td>2.50</td>
<td>32.3</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.0094</td>
<td>0.15</td>
<td>1.21</td>
<td>26.5 ±0.1</td>
<td>94.1 ±0.9</td>
<td>7.85</td>
<td>2.60</td>
<td>33.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0165</td>
<td>0.26</td>
<td>1.16</td>
<td>29.8 ±0.2</td>
<td>94.3 ±0.7</td>
<td>7.93</td>
<td>2.31</td>
<td>29.1</td>
</tr>
</tbody>
</table>
Figure 6.7 Percentages of water mass recovered based on the orientation of the down spout injector \textit{(i.e., directed such that water was injected into the combustor’s exhaust or out of and away from the exhaust)}.

By multiplying the water flow rate through the system by the percentage of water mass not collected in the plastic basin at the end of each experiment, a rate of water mass that has been vaporized can be calculated. The average final water temperature, prior to exiting the down spout, was $94^\circ C$, and at this temperature the latent heat of vaporization for water is most nearly 2.3 MJ/kg. By multiplying the mass flow rate of vaporized tap water by this value provides the total amount of power used for water vaporization. Furthermore, since water temperature was recorded for the tap water flow before entering the heat exchanger around the combustor body and after exiting it, the power required to raise the temperature of the water flow can be calculated. By summing these two power values together and dividing by the input power, the percentage of power recovered (or “used”) by the system can be calculated.
Table 6.4 System thermodynamic analysis.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Test #</th>
<th>Water Flow Rate (kg/s)</th>
<th>Fuel Flow Rate (g/s)</th>
<th>Fuel–Air Equivalence Ratio (φ)</th>
<th>Input Power (kW)</th>
<th>Mass Collected (%)</th>
<th>Mass Vaporization Rate (kg/s)</th>
<th>Power for vaporization (kW)</th>
<th>ΔT across body heat exchanger (K)</th>
<th>Power for raising fluid temperature (kW)</th>
<th>Power Recovery (%)</th>
<th>Average (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>1</td>
<td>0.011</td>
<td>1.20</td>
<td>1.52</td>
<td>56.3</td>
<td>16.7</td>
<td>0.00691</td>
<td>20.3</td>
<td>65</td>
<td>2.91</td>
<td>41.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.010</td>
<td>1.47</td>
<td>1.86</td>
<td>68.9</td>
<td>12.3</td>
<td>0.00877</td>
<td>19.9</td>
<td>65</td>
<td>2.72</td>
<td>32.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.010</td>
<td>1.23</td>
<td>1.55</td>
<td>57.7</td>
<td>18.5</td>
<td>0.00785</td>
<td>17.9</td>
<td>68</td>
<td>2.73</td>
<td>35.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.009</td>
<td>1.19</td>
<td>1.50</td>
<td>55.8</td>
<td>29.1</td>
<td>0.00638</td>
<td>14.5</td>
<td>67</td>
<td>2.52</td>
<td>30.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.010</td>
<td>1.23</td>
<td>1.55</td>
<td>57.7</td>
<td>21.8</td>
<td>0.00759</td>
<td>17.3</td>
<td>67</td>
<td>2.72</td>
<td>34.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.010</td>
<td>1.14</td>
<td>1.44</td>
<td>53.5</td>
<td>38.2</td>
<td>0.00595</td>
<td>13.5</td>
<td>67</td>
<td>2.69</td>
<td>30.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.009</td>
<td>1.49</td>
<td>1.88</td>
<td>69.9</td>
<td>32.3</td>
<td>0.00633</td>
<td>14.4</td>
<td>67</td>
<td>2.63</td>
<td>24.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.009</td>
<td>1.21</td>
<td>1.53</td>
<td>56.7</td>
<td>33.1</td>
<td>0.00625</td>
<td>14.2</td>
<td>68</td>
<td>2.67</td>
<td>29.73</td>
<td></td>
</tr>
<tr>
<td>Out</td>
<td>2</td>
<td>0.017</td>
<td>1.16</td>
<td>1.47</td>
<td>54.4</td>
<td>29.1</td>
<td>0.01169</td>
<td>26.6</td>
<td>65</td>
<td>4.48</td>
<td>57.13</td>
<td></td>
</tr>
</tbody>
</table>
(Note that the second experiment of the “out” condition had a tap water flow rate through the system that was significantly higher than the other tests. Because fluid flow rate directly affects power recovery [see Equation 6.1], the results of this experiment were not considered when considering the average behavior or performance of the system during the “out” condition.)

Recall that in the front-end-coil tests, the power from the conductive transfer of convective thermal energy from the exhaust gas to the fluid flowing through the coil array was about 3 kW. In these experiments, on average 4.6 kW of power were gained by injecting the tap water into the exhaust gas. This represents a 40 to 50% increase in power, compared to the front-end-coil experiments. Furthermore, the average system power usage obtained by injecting the tap water into the exhaust from the super-charged pulsed jet combustor increases by 22%.

Shown in the fifth column from the left in Table 6.4 is the fuel-air equivalence ratio for each experiment. This value was retro-actively calculated for each condition using Equation 6.3. (See Chapter 8, Section 8.2.1 for a more detailed discussion on the fuel-air equivalence ratio.) On average, the fuel-air equivalence ratio for these nine experiments was calculated to be about 1.6 (i.e., fuel rich). If, however, the system operated at an fuel-air equivalence ratio of 1.0 (i.e., stoichiometric) the values for percent power usage (i.e., power recovery) would perhaps improve. For example, if the percent power usage values for each experiment are multiplied by the calculated fuel-air equivalence ratio for that test, the average percent power recovery for the experiments where the tap water was injected into the exhaust improves from about 37% to 60%.

\[ \varphi = \frac{\left( \frac{m_{\text{fuel}}}{m_{\text{air}}} \right)_{\text{actual}}}{\left( \frac{m_{\text{fuel}}}{m_{\text{air}}} \right)_{\text{stoichiometric}}} \]

Equation 6.3 The fuel-air equivalence ratio. See Chapter 8, Section 8.2.1 for a more detailed discussion.
6.5 Summary

As a brine treatment system, the super-charged pulsed jet combustor combines a conductive heat exchanger around its body with the pulsating hot gas from its exhaust to separate dissolved salt from solvent water in hypersaline brines. To determine the power available from the thermal energy in the combustor’s pulsating exhaust gas, the team developed convective and conductive power recovery experiments. When considering the improvement of thermal energy transfer by convection versus conduction, the power of the exhaust gas increases by 50 to 60%. Similarly, by exposing the water flow to the hot pulsating exhaust gas (versus not utilizing it at all), a 22% increase in power is achieved.

It should be noted that for all experiments that used the down spout (“goose-neck”) injector, the team noted that water droplets (perhaps as large as 0.5” [1.27 cm] in diameter) appeared to pass undisturbed through the super-charged pulsed combustor’s exhaust gas. Though this topic is addressed further in Chapter 8 (Section 8.2.2), it is worthwhile noting that observing this behavior may indicate incomplete primary atomization of the liquid, in the exhaust gas, which could reduce convective heat transfer rates. In turn, this could decrease the rate of vaporization, and decrease the power (or energy) recovered. Nonetheless, as previously related, the system proved robust, and the thermodynamic benefits of the exhaust gas were demonstrated.
6.6 References


CHAPTER 7: TESTING THE SYSTEM USING A NOVEL SCREEN ARRAY

7.1 Introduction

The research for this thesis began in earnest in May 2014, when the super-charged pulsed jet combustor was installed by the team at University Park, PA. The initial, fundamental experiments with the system, however, started 14 months earlier. In September 2013, Dr. Cannon, Mr. Thomas Geeza, and the Furness-Newburge team developed a unique salt-water separation experimental setup called “salt-on-screen.” As its name implies, the process used the super-charged pulsed jet combustor to separate dissolved salts from solvent water, whereby a hydrated salt paste agglomerated onto metal mesh screens located near the end of the combustor tailpipe. When the super-charged pulsed jet combustor came to Penn State University, the first experiments conducted used this experimental setup. This chapter provides insight into these “salt-on-screen” collection experiments performed at Penn State and the results thereof.

7.2 Materials & Methods

Because the research related in this thesis is presented in reverse chronological order (i.e., this research occurred before the research presented in Chapters 5 and 6), all of the materials used during these experiments have already been discussed.

At Penn State, the metric used for the “salt-on-screen” experiments was the percentage of the salt, which had been formerly dissolved in water, that was collected as hydrated paste on galvanized, wire mesh screens. Also known as “hardware cloth,” these screens were comprised of 19 gauge (0.912 mm diameter) steel wires welded together to create sheets 24” (0.61 m) tall, and at least 4’ (1.22 m) long, with ½” (1.27 cm) square openings. As shown in Figure 7.1 and
7.2, two identically-sized screens were placed on either side of the combustor body – about 1.5” (3.8 cm) from the outer wall. These ran parallel to the combustor body, in the exhaust region. Each individual piece was approximately 24” (0.61 m) tall by 36” (0.91 m) long. On one side, a metal plate was placed less than half an inch (< 1.27 cm) behind the screens. The screens extended approximately 12” (30.5 cm) above and below the centerline axis of the combustor. Before being secured in place, each dry screen piece was individually weighed.

All experiments conducted with the super-charged pulsed jet combustor at Penn State used a surrogate brine. The salt water used in the tests related in this chapter was created by hand mixing tap water and whole water-softening commercial salt (NaCl) pellets. The percentage of the brine that was salt (by mass) was based on the mass of whole salt pellets that were added to the water.

Brine flows were determined by calibrating a chemical metering pump, prior to conducting experiments.

Brine was injected into the super-charged pulsed jet combustor’s exhaust through a uniquely-shaped, ¼” (0.64 cm) diameter, pipe end. Furness-Newburge flared and bent the end of this pipe such that its final shape was similar to that of a duck’s bill. This so-called “duck bill” injector was positioned so that it injected fluid into the center of the exhaust gas stream coming from the super-charged pulsed jet combustor. Figure 7.2 shows an experimental setup.
After each test, the screens backed by the metal plate were removed and dried in an oven for 45 minutes. (No salt accumulation was ever observed on the screens not backed by the metal plate.) Once dry, the final weights of the screens, which were caked with salt, were recorded.

### 7.3 Results

After receiving and installing the super-charged pulsed jet combustor, six salt-on-screen collection tests were conducted over three days, during June. The purpose of these experiments was to determine the effect of liquid flow rate and fuel mass flow rate on the percentage of salt collected as a hydrated paste onto screens.

The results from the salt-on-screen tests at Penn State are shown in Table 7.1. Three brine flow rates were investigated – 0.021, 0.023, and 0.026 kg/s (0.33, 0.37, 0.41 gpm). These were set by pre-calibrating the chemical metering pump. The two fuel mass flow rates investigated were 0.9 and 1.6 g/s (0.12 and 0.21 lb/min). The operator was responsible for setting the pressure and flow of the propane, while the mass decrease of the fuel source tank before and after each experiment yielded a precise fuel mass flow rate.

As shown in Figure 7.4, no discernable trend was shown for the screen which collected the most salt, relative to its position to the end of the combustor.
### Table 7.1 Results of salt-on-screen collection tests at Penn State.

<table>
<thead>
<tr>
<th>Date</th>
<th>Test #</th>
<th>Brine Flow (kg/s)</th>
<th>Fuel Flow (g/s)</th>
<th>Dried salt mass collected by screen location (g)</th>
<th>Total dried salt mass collected (g)</th>
<th>% of total collected salt by screen location</th>
<th>% of total processed salt collected onto screens</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 4</td>
<td>1</td>
<td>0.021</td>
<td>0.95</td>
<td>Near&lt;sup&gt;a&lt;/sup&gt; 8.5 Far&lt;sup&gt;b&lt;/sup&gt; 19.1</td>
<td>27.6</td>
<td>30.8 Near&lt;sup&gt;a&lt;/sup&gt; 69.2 Far&lt;sup&gt;b&lt;/sup&gt; 4.4</td>
<td></td>
</tr>
<tr>
<td>June 4</td>
<td>2</td>
<td>0.026</td>
<td>0.85</td>
<td>14.5 Far&lt;sup&gt;b&lt;/sup&gt; 8.7</td>
<td>23.2</td>
<td>62.5 Near&lt;sup&gt;a&lt;/sup&gt; 37.5 Far&lt;sup&gt;b&lt;/sup&gt; 3.0</td>
<td></td>
</tr>
<tr>
<td>June 4</td>
<td>3</td>
<td>0.023</td>
<td>0.89</td>
<td>21.2 Far&lt;sup&gt;b&lt;/sup&gt; 2.2</td>
<td>23.4</td>
<td>90.6 Near&lt;sup&gt;a&lt;/sup&gt; 9.4 Far&lt;sup&gt;b&lt;/sup&gt; 3.3</td>
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</tr>
<tr>
<td>June 10</td>
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<td>0.021</td>
<td>1.66</td>
<td>Near&lt;sup&gt;a&lt;/sup&gt; 69.4 Far&lt;sup&gt;b&lt;/sup&gt; 7.3</td>
<td>76.7</td>
<td>90.5 Near&lt;sup&gt;a&lt;/sup&gt; 9.5 Far&lt;sup&gt;b&lt;/sup&gt; 6.2</td>
<td></td>
</tr>
<tr>
<td>June 10</td>
<td>2</td>
<td>0.026</td>
<td>1.51</td>
<td>63.6 Far&lt;sup&gt;b&lt;/sup&gt; 33.9</td>
<td>97.5</td>
<td>65.2 Near&lt;sup&gt;a&lt;/sup&gt; 34.8 Far&lt;sup&gt;b&lt;/sup&gt; 6.3</td>
<td></td>
</tr>
<tr>
<td>June 11</td>
<td>1</td>
<td>0.023</td>
<td>1.66</td>
<td>33.5 Far&lt;sup&gt;b&lt;/sup&gt; 19.3</td>
<td>52.8</td>
<td>63.4 Near&lt;sup&gt;a&lt;/sup&gt; 36.6 Far&lt;sup&gt;b&lt;/sup&gt; 6.4</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Nearest to exhaust end of combustor

<sup>b</sup> Farthest from exhaust end of combustor

---

**Figure 7.3** An image depicting the naming convention used for the left-hand-side screens, which collected salt. A separation between the two screen pieces is shown and exaggerated for clarity. Not to scale.
Figure 7.4 The amount of salt on each of the two left-hand side screens, as a percentage of the total salt collected across both screens. The top figure shows the experiments in order of increasing fuel flow to the combustor (units of g/s; left to right). The bottom shows the experiments in order of increasing brine flow rate (units of kg/s; left to right). Test number and date are shown beneath each column.
As previously noted, hydrated salt only appreciably collected on the screens that were backed by a metal plate. For the Penn State experimental setup, the metal plate was always on the left-hand-side of the super-charged pulsed jet combustor. Consequently, only dry mass gained on those screens was evaluated.

For the lower fuel mass flow rate (0.90 g/s), on average 24.7 grams (0.05 lbs) of salt were collected on the left-hand side screens, across the three brine flow rates investigated. When the average propane mass flow rate increased (to 1.61 g/s), an average of 75.7 grams (0.17 lbs) of salt were collected onto the left-hand side screens across the same three brine flow rates.

![Figure 7.5 Hydrated salt paste on screens after tests.](image)

(a) Near screen, test #2 on June 4th, 14.5 grams of salt (dry).  (b) Near screen, test #1 on June 10th, 69.4 grams of salt (dry); this hydrated paste had the appearance and consistency of shaving cream. Note that the backing plate has been removed prior to taking these photographs.
7.4 Discussion

Overall, less than 10% of the total mass of dissolved salt processed through the system during any of these six experiments agglomerated onto the left-hand side screens. (Recall that the right-hand side screens did not accumulate any significant salt mass, compared to the left-hand side.) Therefore, the primary significance of this research is not as an effective salt-water separation technique; but rather whether or not there is a discernable effect of fuel or fluid flow rates on the percentage of salt collected.

As shown in Figure 7.6, it appears that for a given fluid delivery rate, as the combustor received more fuel, the percentage of salt mass accumulated onto the screens increased.

To further investigate the effect of increasing fuel flow rate on the percentage of salt collected, Table 7.2 and subsequently Figure 7.7 were created. Of the six tests, three have equal brine flow rates. As mentioned, Figure 7.5 indicates that, at a given brine flow rate, if more fuel is fed to the combustor, more salt is collected. Is there, however, a direct linear relationship between the increase in fuel flow rate and the percent of salt separated from the brine and agglomerated onto the screens?

By comparing the percent increase in fuel flow rate for each flow rate to the percent increase in salt collected onto the screens, it can be determined if there is a direct linear relationship between these variables. As shown in Figure 7.4, there does not appear to be a significant linear relationship. However, the evidence of a trend remains.
Figure 7.6 The percent of total salt mass processed during a run which was collected onto both left-hand side screens at different brine flowrates and different fuel (propane) flow rates. Data is segregated by average fuel mass flow rates.
Table 7.2 The effect of increasing fuel flow rate on salt collection onto the screens.

<table>
<thead>
<tr>
<th>Brine Flow (kg/s)</th>
<th>Fuel Flow (g/s)(^a)</th>
<th>Fuel Flow (g/s)(^b)</th>
<th>% Increase in Fuel Flow Rate</th>
<th>% Salt Collection onto screens(^a)</th>
<th>% Salt Collection onto screens(^b)</th>
<th>% Salt Collection Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.021</td>
<td>0.95</td>
<td>1.66</td>
<td>175</td>
<td>4.4</td>
<td>6.2</td>
<td>139</td>
</tr>
<tr>
<td>0.023</td>
<td>0.89</td>
<td>1.66</td>
<td>186</td>
<td>3.3</td>
<td>6.4</td>
<td>192</td>
</tr>
<tr>
<td>0.026</td>
<td>0.85</td>
<td>1.51</td>
<td>179</td>
<td>3.0</td>
<td>6.3</td>
<td>210</td>
</tr>
</tbody>
</table>

\(^a\) For experiments 1 through 3 conducted on June 4

\(^b\) For experiments 1 through 2 conducted on June 10, and experiment 1 conducted on June 11

Figure 7.7 Although there may be a trend, there does not appear to be a significant linear relationship between increasing the fuel flow rate to the combustor and the subsequent increase in the percent of salt mass collected on the screens.
7.5 Summary

An initially informative experimental setup, the effectiveness and usefulness of the salt-on-screen collection tests were limited by energy considerations and the extent of salt collection on the screens. The amount of energy (from fuel) expended to recover the salt on the screens was an order of magnitude greater than that of conventional spray-drying-type systems (i.e., 60 MJ/kg versus 5 MJ/kg). Salt appreciably collected on any surface which disrupted the exhaust gas flow. So, the likely explanation for the synergistic effect of the metal plate is that it deflected hot gas and evaporating brine droplets back toward the metal, mesh screens, on which they settled, the salt nucleated, and the water evaporated.

As shown in Figure 7.8, salt often encrusted the pipe end, plastered the witness plate, and covered any available, dry (or heated) surface. Considering the small masses of salt agglomerated onto the screens, these salt deposits may have been significant.

Another foreseeable difficulty with the salt-on-screen collection method would be graduating to a full-scale, continuous-operation process. If a process like this one was used on an industrial scale, most likely the operation would have to be routinely and frequently halted, and workers would have to manually clean or remove screens for final disposal. Alternatively a complex mechanical array could be developed, whereby hydrated paste could be scraped or brushed from the screens, and segregated from the non-evaporated fluid. In either case, the system setup previously presented in Chapter 5 seems to be more preferable.
Figure 7.8 Salt deposits that were observed but not collected after experiments. (a) shows salt encrusted on the pipe end that was shaped like a duck bill. (b) shows hydrated salt paste that has plastered the plate that backed the screens and a plastic clamp. (c) shows a film of salt that covers some of the end of the combustor’s tailpipe. Considering the small masses of salt collected on the screens (20-100 g), these amounts (especially those shown in (a) and (b)) may have been significant.
8.1 Project Summary

As described and evaluated in Chapter 5, this process can successfully be applied to hypersaline brines. This stands in stark contrast to conventional desalination processes which cannot process wastewaters that have TDS concentrations $\geq 150,000$ mg/L. In addition to performing well with hypersaline brines, when using the experimental setup described in Chapter 5, the majority of the salt remained with the un-vaporized water. This is especially favorable because it implies that the mass of particulate matter that may be mobilized in the air phase should be small.

8.2 Future Research Investigations

In Chapter 2, the power consumption requirements of conventional salt-water separation systems (e.g., reverse osmosis, thermal distillation, etc.) were discussed. As was shown, for brines with TDS concentrations $<100,000$ mg/L, there exist several conventional technologies that can effectively separate dissolved salt from water, using less energy overall than demanded by evaporation. Because these systems, however, are limited by the TDS concentration of the influent brine, the energy they require to evaporate a kilogram of water solvent may be irrelevant when discussing how to remediate hypersaline brines. In contrast, the super-charged pulsed jet combustor has been shown to not be limited by the TDS concentration of the influent brine. Reducing the energy requirement of the super-charged pulsed jet combustor system, however, is still a good goal. The following are some potential ways which may do so.
8.2.1 Moving Equivalence Ratio Closer to Stoichiometric

Ideally all the fuel flowing into a combustor should be fully oxidized. Otherwise it is unused. Similarly, if a carbonaceous fuel is not fully converted to water vapor and gaseous carbon dioxide, combustion is incomplete, and less energy is released compared to complete combustion. Therefore, checking the completeness of combustion in a hydrocarbon-burning unit is important because it impacts the overall system efficiency [1].

In combustion, there exists an air-to-fuel ratio. This air-to-fuel ratio can be simply defined as $\frac{m_{\text{air}}}{m_{\text{fuel}}}$, where $\dot{m}$ represents mass flow rate [2]. Air contains mostly nitrogen and oxygen gas [3]. Oxygen serves as the oxidant in combustion reactions. Accounting for the chemical composition of the air, if the amount of air provided to the combustion reaction in a given system is precisely equal to the amount predicted to be required by the chemical combustion reaction, then the mixture is stoichiometric and the air-to-fuel ratio equals unity.

Literature shows that pulsating combustors have operated at air-to-fuel ratios ranging from 0.95 to 1.10 [4, 5]. In their 1999 paper, Zbicinski, et al., assert that the, “[O]ptimum point [of pulse combustor operation]…corresponds to the stoichiometric fuel/air ratio” [6]. In addition to so-called “optimum operation,” combustion within pulsating combustors is generally kept as close to stoichiometric conditions as possible, to reduce the generation of potentially harmful air emissions [7, 8].

$$\varphi = \frac{\left( \frac{m_{\text{fuel}}}{m_{\text{air}}} \right)_{\text{actual}}}{\left( \frac{m_{\text{fuel}}}{m_{\text{air}}} \right)_{\text{stoichiometric}}}$$

**Equation 8.1** The fuel-air equivalence ratio [9].
The closeness of combustion to the ideal stoichiometric condition can also be characterized as the fuel-air equivalence ratio ($\varphi$), as shown in Equation 8.1. When $\varphi$ is equal to unity, the combustion reaction is stoichiometric; when $\varphi > 1$ the reaction is fuel rich; and if $\varphi < 1$ it is fuel lean [9]. For pulsating combustors, reported fuel-air equivalence ratios range from 0.5 to 1.4, but most units reportedly operate below 1.0 [4, 5, 10, 11].

In his 2007 PhD thesis titled “Mathematical Model of a Mechanically-valved Pulse Combustor,” Dr. Wu provided a short but focused investigation into the effect of the air-fuel equivalence ratio on thrust produced by a pulsing combustor [12]. Dr. Wu investigated the instantaneous thrust developed by his pulsating combustor at air-fuel equivalence ratios 1.12, 1.0 and 0.7. He found no observable difference in the combustion chamber gas pressure amplitude across the three conditions. As shown in Table 8.1, however, the thrust-to-fuel (T/F) ratio was greatest for the 1.12 equivalence ratio condition; but it was not markedly improved over the stoichiometric condition. Citing Zinn (1985) and Putnam (1986), Dr. Wu seems to conclude that energy is conserved and “cyclically steady” pulse combustion is achieved when supplying “a small excess air.”

<table>
<thead>
<tr>
<th>Equivalence Ratio</th>
<th>Oscillating Pressure (Pa)</th>
<th>Exit Velocity (m/s)</th>
<th>Fuel Flow (g/s)</th>
<th>Average Thrust (N)</th>
<th>T/F (N·s/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.12</td>
<td>4000-8000</td>
<td>40-130</td>
<td>0.455</td>
<td>0.762</td>
<td>1.675</td>
</tr>
<tr>
<td>1.00</td>
<td>3446-9163</td>
<td>50-141</td>
<td>0.521</td>
<td>0.855</td>
<td>1.641</td>
</tr>
<tr>
<td>0.70</td>
<td>3571-8280</td>
<td>54-141</td>
<td>0.742</td>
<td>0.878</td>
<td>1.183</td>
</tr>
</tbody>
</table>

38 Dr. Wu calls it the “fuel-air” equivalence ratio in his PhD dissertation, but his discussion of his results and other comments do not match this. For example, when comparing the “1.0” ratio to the “1.12” ratio he says, “Compared with the stoichiometric condition, the pulse combustor has only a small improvement in thrust-to-fuel [T/F] ratio when the air supply was increased.” If he truly referred to a fuel-air ratio, going from “1.0” to “1.12” would indicate a decrease in the supply, not an increase.
As previously discussed, in this work, fuel mass flow rate was determined using a balance during each experiment. Compressed air flow rate was measured visually via an acrylic tube flowmeter. On average, for the experiments conducted herein, the air fuel-air equivalence ratio ($\varphi$) was calculated to most nearly be 1.8. This would indicate that during normal system operating conditions followed in the research related in this thesis, the super-charged pulsed jet combustor was likely being operated at a fuel-rich condition.\textsuperscript{39}

### 8.2.2 Brine Introduction to the Exhaust Gas

Another potential process improvement that may reduce the energy usage of the system is to use a nozzle to induce primary brine atomization. Although nozzle-less atomization is a demonstrated benefit of conventional spray drying using pulsating combustion, during experiments at Penn State University that used the $\frac{1}{2}''$ (1.27 cm) diameter “down spout” or “goose-neck” to injected brine into the exhaust, the team observed that the atomization of the liquid coming in the exhaust was less pronounced than in previous experiments that had used smaller-diameter orifices. Thus it may be that the internal diameter of the down spout was too large, and it injected a volumetric rate of liquid too great to be atomized by the exhaust from the super-charged pulsed jet combustor.

\textsuperscript{39} A more rigorous determination of the true air pressure (which affects specific gravity) in the compressed air line is necessary to refine this calculation, which was done using $\text{SG}_{\text{air}} \approx 1$. 

175
In a brief technology review, Ozer [13] discussed the Unison Drying System – a commercial pulse combustion spray dryer. Hosokawa Bepex used this system to successfully dehydrate liquid solutions that contained dissolved or suspended solids (e.g., food, pharmaceuticals, polymers, organics, and specialty chemicals). In this pulse combustion spray dryer, the fluid to be dried was ejected into the drying chamber at 1 gpm (227 lph) using a ¼” (0.635 cm) outer diameter line with a 1/8” (0.318 cm) internal diameter. In this paper, however, Ozer did not include many critical operating parameters of the Unison Drying System, or the characteristics of the liquid solutions for which the system was deemed successful. To preclude clogging or high pressure steam build up which would stop the flow of brine through the system, the use of fluid transport and delivery lines with internal diameters smaller than 3/8” (0.95 cm) were not used with the super-charged pulsed jet combustor system. Ozer, however, did not report any such problems with the small diameter lines of the Unison Drying System. Therefore, it may be possible to reduce the diameter of the fluid delivery lines in the super-charged pulsed jet combustor system while avoiding clogging and thereby perhaps increasing atomization at high (>0.5 gpm; >113.5 lph) liquid flow rates.

Another possibility, however, is that fluid flow rates during experiments with the super-charged pulsed jet combustor were too high. As Ramanarayanan, et al., state, “It is well known...
that acoustic oscillations could be dampened by spray droplets” [8]. Since these acoustic oscillations are key for atomization in spray dryers that use pulsating combustors, great care should be taken not to overwhelm them with a liquid mass flow which they cannot atomize.

For example, Wu and Mujumdar found that increasing the solution feed rate (10.8, 20.52, and 28.2 kg/h – approximately 0.04, 0.08, and 0.16 gpm) into the drying chamber of their spray dryer that used a pulsating combustor decreased the moisture content of the droplets for a specific range of droplet size (they did not elaborate on if or how droplet size varied with feed rate) [14]. Although they deemed their system to be successful, they found that their system could not fully dry droplets at a solution flow rate of 10.8 kg/h (about 0.04 gpm).

During experiments at Penn State, it was observed that for brine flows >0.3 gpm (.68 lph) water droplets coming from the down spout passed through the exhaust gas stream without being fully atomized. This observation seems to support the droplet-entrainment notion reported by Zinn [15]. Because relative to the high-velocity oscillating exhaust gas from a pulsating combustor the fluid ejected into it is more or less stationary, it is important to determine at what point atomized, liquid droplets will become suspended in the gas, since this transport rate directly correlates to drying.

![Figure 8.2](image.png)

**Figure 8.2** The relationship between particle entrainment factor (η) and combustor oscillation frequencies [15].
efficiency in conventional spray drying [15].

According to Zinn, droplet entrainment can be predicted by an “entrainment factor,” \( \eta = \frac{v_p}{v_g} \), where \( v_p \) represents the amplitude of the droplet velocity and \( v_g \) is the velocity of the gas [15]. The graph shown in Figure 8.2 relates particle entrainment factor to particle diameter for oscillating gas frequencies ranging from 50 Hz to 10 kHz. The closer \( \eta \) is to 1, the more fully the droplet is entrained within the gas phase.

It is possible that during experiments at Penn State, the frequency of the rotating air valve on the super-charged pulsed jet combustor may not have correspond well to the droplet sizes within the exhaust gas. This could explain the relatively low amounts of water vaporized. Consequently, subsequent experiments (not included in this thesis) have investigated: (1) using an atomizing nozzle to consistently produce droplets of uniform size, and (2) varying rotational speed of the air valve.

8.2.3 Combustor Tuning

The resonant frequency of a pulsating combustor depends on the geometry of the body. Although the geometric design of a pulsating combustor is beyond the scope of this thesis, it is important to note that the constant contact of the heat exchanger on the body (which it is wrapped around) is possibly affecting the acoustical operation of the super-charged pulsed jet combustor. Research presented in literature has found that a cooling water jacket around the body of a pulsating combustor may act as an acoustic filter, and by altering the length of the water jacket, pressure amplitude and oscillation may be controlled without changing any other operating conditions [5, 12]. This presents yet another important variable that could affect the
performance of the super-charged pulsed jet combustor system, and will be investigated further in future research.

Another system component which is likely affecting the inherent, acoustical resonance of the super-charged pulsed jet combustor is its rotating, air-delivery valve. To achieve optimal performance, pulsating combustors should be designed such that the time of repeated heat discharge coincides with the point of maximum pressure change in the combustion chamber [29]. As shown in Figure 8.3, matching the timing of the heat release (Q) to the point at which pressure amplitude is greatest, increases the amplitude of the pressure wave, per Rayleigh’s criterion [5, 12, 17]. As noted in Chapter 3, to achieve acoustic resonance, it is critical that pulsating combustors that use mechanically-actuated, externally-controlled rotating mechanical air-delivery valves are timed so that they allow air to pass through into the combustion chamber precisely at the time of lowest pressure (i.e., valve rotation must be perfectly synchronized with the inherent oscillation frequency of the combustor) [18, 19]. If this condition is not achieved, the combustion may be forcibly pulsed, but the combustor may perform sub-optimally. This is why, for conventional units that employ rotating, air-delivery valves, researchers monitor the produced pressure waveforms to tune the unit [20].

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40 Optimal combustor performance can be described as the production of smooth and high amplitude pressure oscillations [6].
Figure 8.3 Four cases of Rayleigh’s criterion, where the amplitude or phase angle of normal combustion chamber pressure (solid line) is altered (the result being shown by the dashed line) by instantaneous energy release (Q) at critical points. Case 1 represents the condition where resonant pressure amplitude is increased by instantaneous energy addition at the correct times, while in Case 2, adding it at the wrong time decreases amplitude [16].
8.3 The Potential to Treat Other Brines

As alluded to in Chapter 2, many petroleum production processes, in addition to hydraulic fracturing, release highly saline brines. For example, brines from coal extraction processes tend to have high TDS concentrations, some reaching 200,000 mg/L [21, 22]. The petroleum production industries, however, are not the only major sources of hypersaline wastewater. Coastal desalination plants are an example of another significant production source of highly saline brines.

While thermal evaporation was historically the preferred seawater desalination method, reverse osmosis is increasing in popularity. According to a 2009 survey by the United Nations Economic and Social Commission for Western Asia (ESCWA), at that time reverse osmosis provided 53% of all the fresh water produced through desalination [23]. Furthermore, worldwide, rates of desalination are expected to increase, as global population increases – especially in arid areas [17]. A 2008 estimate placed the daily rate of global water production from desalination at 25 million m$^3$ (6.6 billion gallons) [24].

One of the key draw-backs of reverse osmosis is the creation of reject brine (also called concentrate, retentate, or blow down) [24, 25]. Post-process, this wastewater is about 30-40% the volume of the flow into the plant, and its salinity is usually 1.5 to 5 times higher than that of the influent seawater [21, 22]. Thus the TDS concentration of reverse osmosis concentrate brine could range from just over 50,000 mg/L to nearly 250,000 mg/L. In some present practices, reject brine is mixed with fresh seawater, so that the TDS concentration of the discharge is not more than 15% above the influent TDS concentration [22]. In addition to being highly saline, retentate commonly contains corrosion products, oxygen scavengers, anti-scaling/foaming/fouling/corrosion additives, and/or acids [17, 22].
Because the cost retentate disposal can represent up to a third of the total desalination cost, reverse osmosis seawater desalination plants frequently select the most inexpensive brine disposal option [24, 27]. Thus, these brines are commonly discharged back into the ocean or dumped into unlined ponds, which may harm the environment [17, 21, 22]. The dehydration of this highly concentrated, saline wastewater using the super-charged pulsed jet combustor technology is a potential alternative.

8.4 Full-Scale Considerations

There are several key subunits that the team anticipates including in subsequent pilot-scale and full-scale version of this system. These are: a drying chamber; a cyclone and/or heated fabric baghouse to capture dried product; a unit to collect particulate matter (i.e., salt) mobilized in the gas phase; and the combustor (or energy source).

The most important aspect of the drying chamber is continual air removal, to keep humidity as low as possible. As Masters wrote, “The addition of heat to a wet droplet is insufficient by itself to promote satisfactory drying. Removal of moisture depends upon the humidity of the surrounding drying air. To maintain high drying rates, cool humid air must be moved from around a droplet and replaced with hot, low humidity air” [26].

Acoustics is an important but lesser-known aspect that must also be considered when designing the drying chamber. Prior to the 1990’s, the most common method of spray drying using a pulsating combustor was to eject the solution inside the combustor’s tailpipe. Researchers found, however, that dryer system performance could be improved by ejecting the fluid into a chamber called an “applicator.” The hot air from the combustor provided energy for solvent evaporation within the applicator, while the pulses of energy caused the chamber to
acoustically resonate, enhancing convective heat transfer rates [15]. Therefore, rather than
drying in the tailpipe (where residence times were extremely short), spraying the feed into the
applicator increased residence time, resulting in better drying performance.

Although the super-charged pulsed jet combustor system has managed to keep most of
the salt out of the air, there will be some solid particles that may be mobilized into the gas phase
within the drying chamber. Consequently, some form of particulate matter collection system
must be applied to the exhaust gas stream emanating from the drying chamber. Common air-
particle separators used as part of conventional industrial spray dryers include cyclones,
electrostatic precipitators, and baghouses [26, 27].

Before going full-scale, the heat transfer from the combustor body and fluid flow rate
should be decoupled. Compared to other drying systems that use pulsating combustors, the heat
exchanger around the body of the super-charged pulsed jet combustor body is unique. Putting a
heat exchanger around the combustor body was insightful because doing so utilized an often
overlooked advantage of pulsating combustors (i.e., excellent radiative and conductive heat
transfer from the body) and reduced the amount of energy lost to the surrounding environment
[15]. However, to prevent solvent vaporization within the coils, brine flow rate through the
system typically exceeded 0.4 gpm (90.8 lph), which may have overwhelmed the atomizing and
vaporization capacity of the exhaust gas, under normal operating conditions. Thus, brine flow
rate, the temperature of the combustor body, and the available energy in the exhaust gas were all
inextricably linked.

To de-couple liquid feed rate through the system from the thermal energy of the
combustor body, Furness Newburge has recently built a two-part heat exchanger, for a second-
generation system. By continuously circulating high-temperature oil in a heat exchanger around the combustor body and then transferring this energy to the brine in a separate heat exchanger, the brine temperature can be controlled by adjusting the oil flow rate rather than by changing the brine flow rate. Also, an oil-to-air heat exchanger was placed in the oil circulation line. Equipped with variable speed fans, this heat exchanger could bleed heat energy from the hot oil, to keep the brine temperature under control without varying or altering the brine flow rate through the system. Future system plans aim to employ any excess thermal energy emanating from the super-charged pulsed jet combustor to heat the drying chamber and particulate emission control system.

8.5 Summary

At the pilot scale, the super-charged pulsed jet combustor has been successfully applied to saline brines with TDS concentrations in excess of 250,000 mg/L. By effectively processing these hypersaline brines, this research has investigated an unexplored but necessary aspect of treating wastewater from the natural gas and petroleum production industries [28]. The successfulness of this system has met an important prerequisite for moving forward with industrial application [19].
8.6 References


186


APPENDIX A

CO-PRECIPITATION USED TO REMOVE RADIUM ISOTOPES FROM WASTERWATER ORIGINATING FROM THE NATURAL GAS PRODUCTION INDUSTRY
Acknowledgements

A forthcoming journal paper is anticipated to contain some of the information included in this appendix. The author gratefully acknowledges the following individuals for allowing him to present the data which was gathered as part of a collaborative effort: Dr. Cesar Nieto Delgado, Maria I. Zermeno Montante, and Mat Brener. The author is honored to have participated in this research, working alongside these talented scientists and engineers. Also, the author would like to thank Hydro Recovery, LP.

Many thanks go to my advisor, Dr. Fred Cannon, for his assistance, guidance, and the use of the liquid scintillation counter.

The author would also like to thank Dr. Adam Redding and Mike Greenwald for their assistance, input, and guidance on the use of the liquid scintillation counter.

As always, I owe all the thanks to my Savior, Jesus Christ. And I am also very grateful to my wife for allowing me to spend extra time on this additional project.
A.1 Introduction

As discussed in Chapters 2, 5, and 8 of the author’s thesis, naturally occurring radioactive material (NORM) is present in significant amounts in wastewater from oil and natural gas production [1-7]. When this wastewater is processed or treated, the NORM therein becomes technologically enhanced (i.e., TENORM), and may require special disposal [7-9]. Although to date both the drilling industry and regulators believe that TENORM from oil and natural gas production wastes pose little risk to workers and the public, this conclusion is changing [10]. Thus any technology or process claiming to remediate flowback and/or produced brines from the natural gas industry must address the issue of TENORM.

There are many radioactive elements which may be present in oil and natural gas wastewater. Primary among these are uranium, radium, and barium [7]. Because uranium is sparingly soluble, its concentration in flowback and produced brines is usually very low [2, 3, 11]. Barium can be present in appreciable amounts; however, it generally forms BaSO$_4$(s) (barite) which inherently poses little risk [3-5, 11, 12].

Among the primary NORM elements found in flowback and produced brines, radium isotopes are of primary concern due to their environmental persistence and known toxicity [13]. When radioactive elements are in solution, water shields humans and the environment from their nuclear decay ionizing energy. Radium, however, tends to co-precipitate with barite, which forms a hard scale on surfaces routinely in contact with oil and gas workers [14-17].

An alkaline earth-metal, radium has properties similar to calcium [18, 19]. Thus, radium biochemically concentrates in bone marrow, with devastating effect [18, 20, 21]. Furthermore, the immediate daughter product of the radium isotope $^{226}$Ra is radon gas ($^{222}$Rn – not to be
confused with $^{208}\text{Rn}$, the daughter product of the $^{228}\text{Ra}$ radium isotope) and radon is a known carcinogen [19, 20, 22].

The most common radium isotopes in natural gas industry wastewater are $^{226}\text{Ra}$ and $^{228}\text{Ra}$ and their daughter products [2, 16-18, 23, 24]. Radium-226 is a daughter product of uranium-238, and radium-228 is a daughter product of thorium-232, as shown in Figures A.1 and A.2, respectively.

Although the activities of radium in produced waters varies widely as shown in Table A.1, levels commonly exceed environmental standards (the combined maximum contamination level [MCL] for $^{226}\text{Ra}$ and $^{228}\text{Ra}$ is 5 pCi/L) [11, 25].

For this paper, it is only necessary to discuss three out of the five known types of radioactive decay: alpha, beta, and gamma [7]. Alpha ($\alpha$) decay is the emission of a helium particle from an unstable

### Table A.1 Activities (pCi/L) of common radionuclides found in produced brines from the oil and gas industry. Adapted from [1].

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Produced water</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{226}\text{Ra}$</td>
<td>0.054–32,400</td>
</tr>
<tr>
<td>$^{228}\text{Ra}$</td>
<td>8.1–4,860</td>
</tr>
<tr>
<td>$^{224}\text{Ra}$</td>
<td>13.5–1,080</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>0.008–2.7</td>
</tr>
<tr>
<td>$^{232}\text{Th}$</td>
<td>0.008–0.027</td>
</tr>
<tr>
<td>$^{210}\text{Pb}$</td>
<td>1.35–5,130</td>
</tr>
<tr>
<td>$^{210}\text{Po}$</td>
<td>0.005–0.17</td>
</tr>
</tbody>
</table>

![Figure A.1 The radioactive decay series for $^{238}\text{U}$ which contains the $^{226}\text{Ra}$ radium isotope (highlighted) [49].](image)

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$^{41}$ 1 Curie (Ci) is $3.7\times10^{10}$ nuclear disintegrations per second [7].

191
The helium atom is comprised of two protons, two neutrons, and two electrons – making it very large [7]. Beta (β) decay is the ejection of a high speed nucleon electron from an unstable nucleus [7]. Gamma (γ) electromagnetic radiation (or decay) is the emission of a gamma photon from an excited nucleus [7].

To compare the energy of these three key types of decay: the energy of a beta particle (0 to 4 MeV) is sufficient to enable it to travel up to one meter in air or penetrate through a ream of paper [7, 28]. (The ²²⁸Ra isotope has a β-emission energy of about 40 keV [27].) Similarly gamma radiation is extremely intense and must be stopped by a sheet of lead or thick plexiglass [7]. Furthermore, gamma electromagnetic radiation typically accompanies alpha or beta particle emission (e.g., in the case of ²²⁶Ra, which is an α-particle and γ-ray emitter) [28]. Despite is high energy (4 to 8 MeV), the large mass of an alpha particle prevents it from traveling more than a few centimeters in air and it cannot penetrate even a sheet of paper [7, 28]. (The ²²⁶Ra isotope has a α-emission energy of 4.8 MeV [26].)
A.2 Current Radium Removal Methods/Techniques

A.2.1 Adsorption

Radium can be removed from water via adsorption on to iron oxides [20, 29, 30]. It has been found that, around pH 6-9, if limited amounts of calcium, barium, and magnesium are present, up to 25% of radium present in iron-rich waters can be adsorbed into ferric hydroxide precipitant [20]. Radium also readily adsorbs to the negatively charged surface of MnO$_2$, at a pH above 2.8 [20, 29].$^{42}$ Manganese oxide coated acrylic fibers are commonly used for radium adsorption for analytical detection [20, 26, 31]. Radium can be adsorbed within the pores of BaSO$_4$-impregnated, activated alumina [20]. It is also reported to adsorb onto carbonate minerals [32].

Radium is the largest group IIA alkaline earth metal and forms a large hydrophobic divalent cation (i.e., Ra$^{2+}$) in water [19]. An obvious issue with Ra$^{2+}$ adsorption is site competition with other alkaline earth elements, especially barium [20, 26]. In a strongly ionic brine, adsorption of Ra$^{2+}$ will be minimal at best. For example, in studies of strong and weak-acid resins, it was determined that cations were eluted in the following order (first to last, left to right): Ra$^{2+}$ $\rightarrow$ Ba$^{2+}$ $\rightarrow$ Sr$^{2+}$ $\rightarrow$ Ca$^{2+}$ $\rightarrow$ Mg$^{2+}$ $\rightarrow$ Na$^+$ [20].

A.2.2 Co-precipitation

Generally it is not feasible to directly precipitate RaSO$_4$(s) or RaCO$_3$(s) because Ra$^{2+}$ concentrations are too low [33]. Thus, co-precipitation with a carrier-metal sulfate (e.g.,

$^{42}$ Eikenberg, et al., found that a pH > 4 was best for 226Ra adsorption onto MnO$_2$-coated discs [26]. As expected, such pH dependence is widely observed [13, 21, 71].
BaSO$_4(s)$ or SrSO$_4(s)$) is common [18, 20]. This treatment technique has been the most widely-applied for decades because it is considered to be both the most cost-effective and most robust means of removing radium from water [23, 33].

The specifics of co-precipitation are complicated. The process may be governed by surface adsorption (via ion exchange), incorporation of the trace metal into the carrier lattice (substitution), mechanical enclosure within a solid crystal (occlusion), or all of these simultaneously [20, 33-35]. The core principle of co-precipitation, however, can be best summed up in the statement, “[It is] the simultaneous removal of both the tracer and carrier constituents from an aqueous solution without regard to the specific mechanisms involved” [36].

The best way to define co-precipitation would be that it is the formation of substitutional solids in which a tracer metal (e.g., radium) substitutes for the carrier metal [37, 38]. Substitutional solids can be formed by two isostructural compounds [37]. Radium sulphate is isostructural with anglesite (PbSO$_4$), celestite (SrSO$_4$), and barite (BaSO$_4$) [37].

Because barite has such a low solubility (pK$_{sp}$ = 9.96 at 20°C), it is a common scale found on oil and natural gas equipment and pipes [15, 38]. Furthermore, due to its physiochemical similarity between radium and barium (Ba$^{2+}$ ionic radius = 1.36 Å, Ra$^{2+}$ = 1.43 Å), radium is the main radioactive element found in barite scale [15, 17, 39]. The simplified reaction is as

\[
\text{BaSO}_4 + \text{Ra}^{2+}(aq) = (\text{Ra, Ba})\text{SO}_4 (s)
\]

\[
\text{SrSO}_4 + \text{Ra}^{2+}(aq) = (\text{Ra, Sr})\text{SO}_4 (s)
\]

**Equation A.1** Distribution equation for sulfate-based co-precipitation of soluble radium a carrier ion (M) [18].

\[
\frac{\text{RaSO}_4}{\text{MSO}_4} = K_d \frac{\text{Ra}^{2+}}{\text{M}^{2+}}
\]

43 The $K_{sp}$ for RaSO$_4$ is $10^{-10.38}$ [70].
follows: \((\text{excess})\text{Ba}^{2+} + (\text{trace})\text{Ra}^{2+} + \text{SO}_4^{2-} = (\text{Ra,Ba})\text{SO}_4(s)\) [20].

Barite solubility and precipitation in brines has been experimentally studied over a wide range of pressures and temperatures [38]. The degree of co-precipitation is defined by distribution constants (see Equation A.1) [18]. In a dilute solution, the theoretical thermodynamic distribution constant \(K_D\) for co-precipitation of \(\text{Ra}^{2+}\) in barite is about 1.5 and is 237 to 280 for celestite [18, 40]. (It is important to note, however, that these partition coefficients are highly solution dependent [18, 40].) Nonetheless, although barite is most common, celestite is another viable carrier for \(\text{Ra}^{2+}\) with a potentially much higher removal efficiency (see Equation A.2).

A.3 Present Fate of Oil and Natural Gas Wastes

Presently, most oil and natural gas wastewater is either reused or injected into licensed wells for disposal [40-44]. As discussed in Chapter 2, until about 2011, natural gas flowback and produced brines in PA were sent to WWTPs and POTWs, which were incapable of adequately remediating these wastewaters [42, 45]. Although this practice has ended, the fate of the persistent radionuclides discharged from these plants into surface waters is an on-going concern [10].

A potential problem with reinjecting oil and natural gas wastewater into Class II injection disposal wells is that the extreme salinity of the brines keeps radium in solution [10]. (As mentioned, this is due to the extreme ionic competition between \(\text{Ra}^{2+}\) and other mono and multivalent cations for adsorption sites). Thus, should there be any subsurface fluid migration to overlying fresh water aquifers, radioactive contamination would be expected.
When solids (e.g., scales, sludge, cuttings, tailings, etc.) are produced or collected from natural gas production they are landfill [22]. Provided that radiation monitoring alarms are not tripped at the municipal solid waste (MSW) disposal sites, these solid wastes are generally landfilled. The disposal of TENORM is a “gray area,” however, because neither the EPA nor the US Nuclear Regulatory Commission (NRC) regulates NORM waste from oil and natural gas production [17, 24]. Thus it falls to the states.

In Pennsylvania, solid waste processing and disposal facilities must monitor for gamma radioactivity. Although most radioactivity alarms at these sites are triggered by solid waste coming from medical facilities, there have been instances where solid waste from natural gas operations has set them off [46]. For action level one, PA alarms are set to 10 μR/hr above background (60 mrem/yr or 4 to 12 μR/hr) at 50 keV or higher [7, 46]. The criteria for the radioactive contamination being considered “action level two” is the detection of radioactivity of 500 μSv/hr (50,000 μR/hr) or higher from “any other surface” of the waste or “on the outside of the vehicle” [46]. If the amount of radioactive material is sufficiently small (≤1 m³), gamma radiation is less than 0.5 μSv/hr (at 5 cm away), and the activity from all the radium isotopes is ≤ 0.5 pCi/g, then the DEP may authorize immediate disposal [46]. The effectiveness of these methods and the applicability of these units is questionable because the measurements are highly sensitive to the distance from which they are taken and only consider gamma electromagnetic radiation (which many TENORM elements do not emit). Furthermore, measuring, quantifying and comparing radioactivity is difficult because of the difference between dose (i.e., biological

---

44 A 1999 USDOE study, however, concluded that states should not allow solid waste with ²²⁶Ra activity above 50 pCi/g in municipal solid waste landfills [22]. Also, the USDOT does regulate NORM-containing wastes with a specific activity ≥ 2pCi/kg.
45 At 5 cm, at reading of 10 μR/hr correlates to 0.034 μCi of ²²⁶Ra (and daughter isotopes); whereas at twice that distance, 10 μR/hr is equal to 0.14 μCi. Similarly for 500 μS/hr, at 5 cm away it is 193.6 μCi ²²⁶Ra, and at 10 cm it is 774.5 μCi.
effects of nuclear disintegration) and activity (i.e., nuclear disintegration per unit time per volume of radioactive material) units [47].

Although “treatment” of flowback and produced brines in WWTPs and POTWs has stopped in PA, there are industrial facilities dedicated to treating this wastewater [18, 49]. Some rely on chemical precipitation, while others use thermal distillation to process these fluids. A 2009 estimate stated that a one million gallon a day evaporation plant, treating hydraulic fracturing wastewater, would generate about 400 tons of salt waste daily [41]. If the NORM is not removed prior to this evaporative process, it will remain with the solids. While some companies may be able to dilute this solid waste and dispose of it in nearby MSW landfills, such a practice raises questions about radioactivity accumulation and eventual radon gas emissions [22].

Unfortunately, the alternative may not be better. Generally, best practice is to minimize the amount of radioactive material produced [2]. Treatment facilities could concentrate the TENORM into sludge, and dispose of it in permitted landfills [20]. As pointed out by Zhang, et al., however, the radioactivity from radium in precipitate sludge would be at least an order of magnitude above the radioactivity limits of MSW landfills [18]. This is in agreement with the data reported by Parmaksız, et al. [2]. Thus although the volume of the waste decreases, the radioactivity increases, requiring greater isolation of the waste [17]. Sometimes, however, the uncertainty of the unknown (i.e., the long-term effects of the accumulation of radionuclides in landfills) is worse than the challenges of the known (i.e., safe disposal of concentrated, radioactive waste).
A.4 Rationale for this study

In tandem with “remediating” oil and natural gas wastewaters using a novel drying process, PSU researchers also investigated aqueous precipitation reactions in these hypersaline brines. Due to the extremely high ionic strength and complex composition, predicting activity coefficients, which are critical to modeling chemical precipitation reactions, is extremely complicated. As both research topics progressed, it became important to investigate potential methods for removing radium from this wastewater. Furthermore, although radium is easily removed via co-precipitation in solutions with low ionic strength, additional research on its removal in hypersaline brines is useful [32]. Conducting lab-scale precipitation reactions can provide useful data for predicting full-scale behavior and costs (e.g., reactor volume, radioactivity of the sludge and residual solution, necessary chemical addition, etc.) [9].

A.5 Measuring $^{226}$Ra removal via $^{228}$Ra

NORM exists in flowback and produced brines because it is found in the Earth’s crust [7]. The types and concentrations of NORM brought back to the surface primarily depend on the geological structure of the subterranean hydrocarbon reservoir [2]. Thus, the concentrations of radium in wastewater will vary based on the amounts of uranium and thorium at particular locations [2, 20]. Although they are both radium isotopes, $^{226}$Ra and $^{228}$Ra have different parents, and therefore their concentrations are not technically correlated.

Typically more $^{226}$Ra than $^{228}$Ra is present within oil and natural wastewaters. There are several reasons for this, and one is alpha recoil. Although radium is generally considered to be insoluble in water, the high energies of alpha recoil from $^{226}$Ra decay make it slightly more

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46 A referred journal publication on this topic authored by PSU researchers is pending.
soluble [20]. When the alpha particle is ejected from the unstable nucleus during alpha radioactive decay, the remaining nuclide recoils directly into water molecules with an energy \(10^4\text{–}10^6\) times greater than that of common chemical bonds [20]. Thus alpha recoil makes \(^{226}\text{Ra}\) slightly more soluble than \(^{228}\text{Ra}\).

The degree of secondary enrichment of uranium at a particular location determines whether \(^{226}\text{Ra}\) or \(^{228}\text{Ra}\) is the dominant isotope in solution (i.e., when, \(^{228}\text{Ra}\) is generally the dominant Ra isotope in solution, primarily due to the higher natural abundance of Th over U) [20]. Additionally, \(^{228}\text{Ra}\) has a significantly shorter half-life (\(T_{1/2, 228\text{Ra}} = 5.7\) years, versus \(T_{1/2, 226\text{Ra}} = 1,622\) years). Thus, the concentration of \(^{228}\text{Ra}\) decreases much faster than that of \(^{226}\text{Ra}\) [48].

Although also sparingly soluble, uranium-238 (the parent of \(^{226}\text{Ra}\)) forms soluble complexes with carbonates under oxidizing conditions and can be transported by groundwater over long distances [20]. Under reducing conditions, uranium precipitates from groundwater and can be concentrated in secondary deposits [20]. Thus, \(^{226}\text{Ra}\) levels in wastewater are likely to range widely and can be very high at sites of \(^{238}\text{U}\) enrichment [20]. Because thorium-232 is extremely insoluble and immobile in groundwater or in-situ brines (unlike uranium), subterranean \(^{228}\text{Ra}\) concentrations generally do not vary as widely as those of \(^{226}\text{Ra}\) [20].

To-date, the only water-quality parameter that correlates with radium concentration is total dissolved solids (TDS) [13, 20]. For produced brines, this may be due to the extreme competition between Ra\(^{2+}\) and other divalent cations for adsorption sites on subterranean minerals in high ionic strength fluids [49]. In other words, more ionic competition (which
increases with rising TDS, above a certain threshold) for adsorption sites keeps radium in solution [29]. As shown in Figure A.3, this is a commonly observed trend.

There are several techniques for determining radium concentration in water. One of the simplest is liquid scintillation counting (LSC or LSA – see Sections A.6.3 and A.7.2 below) [53]. At PSU, the capability of measuring beta radioactive decay via LSC existed, and was reasonably straight-forward. Conversely, determining the concentration of radionuclides undergoing alpha decay or emitting gamma electromagnetic radiation was prohibitively difficult, required a large sample volume, and a long sample incubation time period (see Sections A.6.4 and A.7.1 below).

Due to physicochemical similarities between $^{226}\text{Ra}$ and $^{228}\text{Ra}$, it is assumed that the degree of $^{228}\text{Ra}$ removal could be an indirect measure of $^{226}\text{Ra}$ removal. In examining groundwater in South Carolina, King, et al., found that “despite lithological differences” there appeared to be a “roughly parallel” distribution between $^{226}\text{Ra}$ and $^{228}\text{Ra}$ [48]. Clifford and Sengupta both wrote that, “Chemically, the isotopes of radium are indistinguishable. Thus, removal of Ra-226 also means equal removal of Ra-228” [19, 20]. Consequently, in

![Figure A.3 The log TDS versus log radium concentration for water from the Marcellus Shale (red squares) and non-Marcellus Shale (blue circles). As shown, there is a linear upward trend between radium concentration and TDS. ND stands for not-detected [49].](image-url)
consideration of the available radium-determination analytical techniques, LSC was selected as the primary method for determining treatment effectiveness.

A.6 Materials

A.6.1 Wastewater from Hydraulically Fractured Shale Gas Wells

A 5 gallon (18.9 L) bucket (see Figure A.4) of wastewater (i.e., an indiscriminate combination of flowback and produced brine) from the natural gas industry in PA was proved by a hydro fracturing brine holding facility in PA. After being filtered through 0.2 μm PES syringe filters (VWR International, LLC; Radnor, PA) the wastewater was analyzed and found to have a TDS concentration of 136,700 mg/L, pH of 6.8, and TALK of 0.16 mmol/L. Its density was 1.13 g/mL. ICP-AES results from a Perkin-Elmer Optima 5300 UV for key elements in this filtered wastewater is shown in Table A.2.

A.6.2 Particle Suspensions

Stock solutions of MnCl₂, KMnO₄, BaCl₂, SrCl₂, FeCl₃ and Na₂SO₄ were prepared from reagent grade chemicals, at concentrations close to saturation. These

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>27,564</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>11,498</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>6,252</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>3,857</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>811</td>
</tr>
<tr>
<td>K⁺</td>
<td>277</td>
</tr>
<tr>
<td>S⁰</td>
<td>245</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.13</td>
</tr>
<tr>
<td>Zn⁺</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Figure A.4 Wastewater from the natural gas industry. Oil can clearly be seen floating on the top.
solutions were used to prepare suspensions, which were made by mixing dropwise while stirring. All suspensions were prepared minutes before use, to prevent agglomeration of the particles. The following are the chemical reactions which created the suspensions of solid particles desired:

\[
\begin{align*}
\text{MnO}_2 & \quad 3\text{MnCl}_2 + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2(s) + 2\text{KCl} + 4\text{HCl} \\
\text{BaSO}_4 & \quad \text{BaCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{BaSO}_4(s) + 2\text{NaCl} \\
\text{SrSO}_4 & \quad \text{SrCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{SrSO}_4(s) + 2\text{NaCl} \\
\text{Fe(OH)}_3 & \quad \text{FeCl}_3 + \text{NaOH} \rightarrow \text{Fe(OH)}_3 + \text{NaCl}
\end{align*}
\]

**A.6.3 Liquid Scintillation**

A common difficulty in measuring radioactivity in liquids is that the radioactive decay energy is quickly absorbed by the water. Thus radioactive decay particles (e.g., alpha or beta particles) cannot reach the detector [50]. Therefore an alternate technique is required to measure their presence in water samples. In general, liquid scintillation counting fulfills this role [7].

Around 1950, the discovery that aromatic compounds absorbed energy from radioactive decay and converted it into light led to the development of liquid scintillation counting (LSC; also called liquid scintillation analysis, LSA) [51-53]. LSC utilizes a special scintillation fluid (often called a cocktail), comprised of organic solvent, emulsifier (also called surfactant), and fluor\(^47\) (or organic scintillator) [50, 51]. The scintillation fluid absorbs the energy from radioactive decay as heat, ionization, and excitation [50]. Irradiated solvent molecules release UV light photons, which are absorbed by the solute fluor molecules [50]. The excited scintillator

\(^{47}\) Fluors are the organic compounds which cause fluorescence or emission of photons when excited by energy from radioactive decay [51].
in turn emits a flash of blue light which can be counted [50]. These photo events are detected by a photo multiplier tube (PMT) and converted to an electronic signal, which can be counted [7] [51].

In this research, a non-toxic biodegradable LSC solution called EcoLume™ (MP Biomedicals, LLC (Solon, OH)) was used. According to the manufacturer, this cocktail is suitable for use with solutions with moderate to high ionic strengths. A LKB Wallac 1217 Rackbeta Liquid Scintillation Counter (Wallac Inc., Gaithersburg, MD) was used to count the light flashes resulting from the radioactive decay events.

**A.6.4 Gamma Spectrometry to determine γ radiation**

Unlike LSC, no cocktail is needed to conduct gamma spectrometry. The gamma rays are sufficiently strong to reach a sensitive detector through water. In gamma spectrometry, the energy wavelength (keV) and count of nuclear decay events over a specific length of time are recorded, as shown in Figure A.5.

For the samples analyzed in this case, they were contained in 1 L polypropylene Marinelli beakers.

Figure A.5 An example gamma spectrum from the publication by van Beek, *et al.* [55]. Notice the two much stronger peaks for $^{214}$Pb versus the single peak for $^{226}$Ra.
(Model 130G-E) from Ga-Ma & Associates, Inc. (Ocala, FL), and the analysis time in the detector was 24 hours per sample. The counts at specific energies are compared to known emission energies from specific radioactive isotopes to determine the activity or concentration of specific species in the liquid. For the samples analyzed in this study $^{226}$Ra activity was measured by the average of the activities of its daughter products $^{214}$Pb (at 295 and 352 keV) and $^{214}$Bi (at 609 and 1120 keV). This is commonly done due to potential interference between $^{226}$Ra (186 keV) and $^{235}$U (185.7 keV) [2, 53, 54, 59].

### A.7 Methods

#### A.7.1 Gamma Spectrometry

All samples for gamma spectrometry analysis were aged for at least 21 days, to allow the short-lived $^{224}$Ra alpha-emitting isotope ($t_{1/2, ^{224}Ra} = 3.64$ days) to completely decay [20, 29]. This also allowed for the $^{222}$Rn and the $^{226}$Ra activities to come to equilibrium [20, 54]. The half life of $^{222}$Rn is 3.82 days, while the half life of $^{220}$Rn is a mere 50 seconds, rendering it less a threat than the radon-222 isotope [20]. The filled Marinelli beakers were then submitted for analysis, and the results were returned as activities in units of pCi.

One and a half liters of filtered hydrofracturing wastewater was combined with 100 mL of a SrSO$_4$ liquid particle suspension with a concentration of 152 g/L. This yielded 1.6 L of a solution with a SrSO$_4$(s) concentration of 9.5 g/L. This stirred for six days, before being allowed to settle, and separating the solids and liquid via filtering.
A.7.2 Liquid Scintillation Counting

As discussed in Section A.6.3, LSC measures the radioactivity in a liquid sample by counting light flashes emitted by organic fluor molecules excited by energy from radioactive decay. As shown in Figure A.6, the emitted light photons are detected by at least two PMTs and converted to electrons, which can be counted [50, 51]. Thus radioactive decay is reported in units of “counts” per time – usually counts per minute (CPM) [7].

There are some nuances with liquid scintillation counting, specifically units’ counting efficiencies, luminescence, and quenching [51]. Quenching occurs when photons (color quenching) and/or nuclear decay energy (chemical quenching) is absorbed by either the sample solution (which often contains many other chemical compounds) or the cocktail solvent [51]. Of the three types of quenching (the third is ionization quenching), chemical quenching is the most common and has the greatest impact [51].

Figure A.6 The liquid scintillation (LSC) process for a radionuclide undergoing beta decay. Note that even though only one photomultiplier tube (PMT) is shown, typically multiple are used [51].

Figure A.7 The chemical precipitation reaction in two, 20 mL scintillation vials. In the vial on the left, it is complete. In the vial on the right, the precipitate has not yet settled.
Starting with filtered wastewater, 15 mL of filtered hydraulic fracturing wastewater was mixed with 2 mL of a pre-made suspension of particles of MnO₂, Fe(OH)₃, BaSO₄, or SrSO₄ in a 20 mL glass scintillation vial. The concentrations of the 2 mL particle suspension additions were such that, when mixed with the wastewater, the concentrations of particles ranged from 0.01 to 50 g/L. The mixture was stirred for at least 24 hours at room temperature (25°C).

After the reaction time, the solution was filtered with a 0.2 μm syringe filter to remove any solids. One milliliter of the filtered samples were mixed with 19 mL of EcoLume™ LSC cocktail. Because of concerns regarding quenching and sample cloudiness (see Figure A.8), this ratio was carefully, experimentally determined. (The procedure used will be discussed at the end of this section.)

Once prepared, each sample sat for 24 hours prior to being analyzed by the LKB Wallac 1217 Rackbeta LSC unit. When samples were ready for analysis, they were placed into plastic racks which were automatically fed through the machine. At each sample location, the rack stopped, and the 20 mL glass vial was lifted up into the detector chamber where it remained for 10 minutes.

In each rack, a “blank” 20 mL vial was included

\[
CPM_{\text{net}} = CPM_s - CPM_{\text{bkg}}
\]

Equation A.3 The equation used to correct for background during LSC sample analysis, where \( CPM_s \) is the value returned by the LSC unit [51].
as well as a vial containing only DI water. In order for the blank to have the same level of quench as the actual samples, it was comprised of 1 mL of DI water plus 19 mL of EcoLume cocktail. Analyzing this blank allowed background count rates (CPM_{bkg}) to be determined, and the true sample count rate (CPM_{net}), using Equation A.3 [51]. Samples were immediately re-tested two additional times, to provide triplicate CPM_{s} values for each sample.

Because $^{228}$Ra has a relatively short half-life and precipitation reactions were frequently separated by days, the activity of a treated sample was compared to a blank sample of the same age. Both samples were analyzed on the same day, within minutes of each other.

As mentioned, there are several key considerations in analyzing radioactive samples using LSC. First is the ratio of scintillation cocktail to sample. Second is the amount of time which the sample and cocktail are allowed to come to equilibrium with each other. Third is the counting efficiency.

As shown in Figure A.9, as the amount of filtered wastewater added to scintillation fluid increased, so did raw CPM returned by the LSC unit. This observation is supported by the data which shows that combining distilled, deionized water with cocktail, regardless of concentration, did not appreciably increase raw CPM (or CPM_{s}), as shown in Figure A.9. This makes intuitive sense, since there is a higher concentration of radioactive isotopes when more wastewater is present. There are limitations, however, to how much sample can be added to cocktail. For example, as previously noted, for the EcoLume™ cocktail used in this study, the manufacturer recommended that the addition of radioactive sample be no more than 10% the volume of the total, combined mixture.

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48 Ideally, the blank should not only contain the same volume of sample and cocktail but the sample should also contain all the same chemical constituents as the radioactive sample – minus the radionuclide of interest [51].
Furthermore, as sample concentration increases, counting efficiency decreases. Therefore, the minimum amount of sample should be employed to achieve a relevant activity measurement, without overloading the PMT or fluor cocktail.

In conjunction with experimentally determining the appropriate ratio of LSC solution to sample, experiments were conducted to evaluate the influence of sample addition percentage and residence time on raw CPM. As shown in Figure A.10, allowing the mixture of scintillation cocktail and wastewater to sit for 24 hours before analyzing with LSC yielded higher CPMs. Again, this makes intuitive sense, as the hydrofracturing wastewater has more time to diffuse within the cocktail. Because LSC is affected by the location of the light flashes relative to the PMTs, the more uniform the sample distribution, the truer and higher the CPM should be.

Figure A.9 The effect of sample percentage on raw counts per minute (CPMₜ) returned by LSC, when adding DI water and hydrofracturing wastewater (HFWW) to the scintillation cocktail.
Ultimately, a 5% ratio of wastewater to cocktail was selected. This ratio was both sufficiently below the scintillation fluid manufacturer’s recommended maximum limit and also yielded a 45 CPM difference between the radioactive sample and the DI water (see Figure A.9). Furthermore, 24 hours was selected as the residence time for samples to undergo, between combining wastewater and cocktail and subsequent LSC analysis.

An inherent limitation of this low sample addition, however, was a low CPM output. To address this, any sample results below 50 CPMs were retested at a 10% sample to cocktail ratio to corroborate the result.

Figure A.10 The effect of the percentage addition of hydrofracturing wastewater (HFWW) to scintillation cocktail and equilibrium times, on raw counts per minute (CPM$_s$) returned by LSC.
A.8 Results

A.8.1 Liquid Scintillation to determine β radioactivity

As noted, the goal of conducting LSC was to quickly compare the effectiveness of different water treatment techniques. Consequently, for each analysis event the counts per minute were normalized against a blank. This yielded the relative reductions in radioactivity \( \frac{C}{C_0} \), shown in Figure A.11 below.

Based on the responses of decreased emissions of beta particles originating from radioactive decay, it seems clear that the beta decaying radioactive elements more thoroughly co-precipitate with SrSO\(_4\) than MnO\(_2\), Fe(OH)\(_3\), or BaSO\(_4\). The removal performance of SrSO\(_4\) is significantly higher than BaSO\(_4\) – at an addition of 5 g/L, 74% of the β-decaying elements had been removed by SrSO\(_4\), compared to 18% removal by BaSO\(_4\), or 45% removal by MnO\(_2\). According to Figure A.11, approximately 4 g/L of SrSO\(_4\) is required to achieve about 60% removal of the β-decaying isotopes, compared to 26.6 g/L of BaSO\(_4\) for the same removal.
Figure A.11 Relative reduction in radioactivity of mixtures of hydrofracturing wastewater and cocktail (C/C₀) with increasing concentrations of co-precipitants (MnO₂, BaSO₄, Fe(OH)₃, SrSO₄). Reaction time is 24 hours.
A.8.2 Gamma spectrometry

To determine the concentration of $^{226}$Ra in liquid samples three batteries of analysis using gamma spectrometry were conducted. The first was three, one liter samples of unfiltered wastewater straight from the PA brine impoundment facility. (As shown in Figure A.1, this raw brine had a floating, oily scum on its surface, and contained particulate matter.) The background of the gamma spectrometry unit was found to be 139 pCi/L. Without subtracting background, the average activity of $^{226}$Ra in the wastewater was found to be nearly 7,000 pCi/L.

During the second test, a liter of wastewater from another PA brine facility (called “Facility B”; which had been filtered using a 0.5 μm pore diameter filter) was analyzed in addition to a liter of wastewater from “Facility A” (which had been filtered through a 0.2 μm filter). The primary purpose of this analysis was to compare the $^{226}$Ra activity between a filtered and unfiltered liter of wastewater, as radium is frequently found in particulate matter [20].

<table>
<thead>
<tr>
<th>Source</th>
<th>Filter Pore Diameter (μm)</th>
<th>Treatment</th>
<th>$^{226}$Ra Activity (pCi/L)</th>
<th>Background (pCi/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>none</td>
<td>none</td>
<td>5,643</td>
<td>139</td>
</tr>
<tr>
<td>A</td>
<td>none</td>
<td>9.5 g/L SrSO$_4$(s)</td>
<td>760</td>
<td>8</td>
</tr>
</tbody>
</table>

Table A.2 Results of gamma spectrometry analysis conducted on hydrofracturing wastewater stored at different locations, and following different filtering or co-precipitation processes.

Depending on unit shielding, background is known to be high for gamma spectrometry [31, 54].
these analyses, the unit’s background was 7 pCi/L. Without subtracting background, the activity of $^{226}$Ra for the wastewater from facility B was nearly 9,800 pCi/L, and for the filtered wastewater it was about 7,400 pCi/L, which correlated very well to the average 7,000 pCi/L $^{226}$Ra activity found in the first three unfiltered water samples from the same location. This confirmed that filtering through a 0.2 μm membrane did not appreciably remove radium.

The third and final gamma spectrometry analysis conducted was performed on a one liter sample of filtered wastewater that had been treated with the addition of SrSO$_4$(s) at a concentration of 9.5 g/L. The unit’s background was 8 pCi/L. Without subtracting background, the $^{226}$Ra activity in this treated sample was found to be 760 pCi/L.

A.9 Discussion

In general, the activity of $^{226}$Ra in the wastewater does not appear to vary significantly, based on whether or not it was filtered. Regardless whether the samples were unfiltered (and an oily sludge with solids was observed to sit atop the 1 L sample) or they were filtered through a 0.2 μm membrane, the activity of $^{226}$Ra remained steady around 7,000 pCi/L. By comparison, after adding SrSO$_4$(s) at 9.5 g/L, thoroughly mixing and separating the precipitate from the supernatant, the activity in the wastewater drops to 760 pCi/L – an 89% activity reduction.
According to the data collected using relative LSC measurements, however, for an addition of SrSO₄(s) to a concentration of 9.5 g/L in the filtered wastewater, an activity reduction of 99.6% would be expected (see Figure A.13).[^50] There are several possible reasons for this. First is the inherent potential error in the analysis and units. For example, Zhang, et al., found that their α LSC and gamma spectrometry results for $^{226}$Ra could differ by up to 7% [18]. This is similar to the 10-11% difference observed in this study.

![Graph](https://via.placeholder.com/150)

**Figure A.13** Expected radium activity reduction from SrSO₄(s) addition, based on LSC data. The $^{226}$Ra activity reduction results for a 9.5 g/L SrSO₄ addition, determined using gamma spectrometry, are also shown for comparison.

[^50]: The LSC normalized radioactivity reduction curve can be described by the polynomial equation $y = 0.0098x^2 - 0.1956x + 0.9781$ at an R² of 0.9976, where x is the addition of SrSO₄. See Figure A.13.
Perhaps most importantly, however, is the unknown relationship between $^{226}$Ra and $^{228}$Ra. Recall that although some studies have found their concentrations to be linked, both radium isotopes come from distinctly different parent products. Furthermore it has been found that $^{228}$Ra concentration in groundwater cannot be predicted by $^{226}$Ra analysis (and the converse should be true, as well) [57]. Consequently, the reduction in beta decay activity in water samples (largely attributed, in this study, to $^{228}$Ra) may not directly correspond to the amount of $^{226}$Ra in the sample.

It should be noted, however, that (1) only one 1 L precipitation reaction followed by gamma spectrometry analysis was conducted; and (2) a 10-11% difference is similar to that found in another study, where $^{226}$Ra concentration was explicitly measured by α LSC and γ spectrometry. Thus, the findings of this research seem reasonable and valid.

All co-precipitation treatments investigated reduced the relative activity of the wastewater. The relative radioactivity decreases, however, with a much smaller addition of SrSO$_4$ or MnO$_2$ than with the traditionally-preferred BaSO$_4$, given the same reaction time. This is surprising since celestite’s solubility limit is below barite’s and BaSO$_4$ is known to form faster than SrSO$_4$ [18, 38]. Interestingly, Kudryavskii and Rakhimova did not observe radium absorption with barite beyond 60%, for a short contact time of 30 minutes at about room temperature [36]. They attributed this, however, to their short reaction time, which they believed to prevent effective sorption and exchange.

Another potential explanation for the difference in this study could be the potentially high uptake of barium when forming celestite [14]. Barium has beta emitting isotopes (e.g., $^{133}$Ba) [60, 61]. In the case of the wastewater from Facility A, used in this study, the concentration of
Ba\(^{2+}\) was slightly less than twice the concentration of Sr\(^{2+}\). Thus, when adding barite, the Ba\(^{2+}\) already in solution is most likely not removed to the same degree as when adding SrSO\(_4\) or MnO\(_2\). Therefore, the relative radioactivity of the sample could remain high. If a sufficient amount of SrSO\(_4\) is added, however, it appears that all the beta decaying radioactive elements co-precipitate with it.

**A.10 Conclusions**

Although this study found that sample radioactivity (predominantly attributed to radium) can be most efficiently removed using SrSO\(_4\), the use of BaSO\(_4\) is more common and historic. There are, perhaps, two key reasons for this. First, the generation or acquisition of SrSO\(_4\) may be prohibitively difficult. Although sodium sulfate is inexpensive and readily available, like barium chloride, strontium chloride is a hazardous chemical [57, 58]. Additionally, though SrSO\(_4\) is naturally occurring and can be mined, according to the USGS as of 2012 no active mines exist [28, 59].

Most likely the reason which co-precipitation with barite is predominant is because flowback and produced brines often contain high concentrations of barium [1, 3]. Thus, simply adding a sulfate compound should form BaSO\(_4(s)\) (among many other products), simultaneously also removing suspended NORM. This could be accomplished by blending with acid mine drainage (AMD) emanating from abandoned coal mines in PA, which generally has a high concentration of sulfate [60, 61].

---

51 In 2012, the cost of celestite was about 50 USD per metric ton [61].
52 Though they can also harbor a high concentration of strontium [75].
53 Maria I. Zermeno Montante and Dr. Cesar Nieto Delgado investigated this topic and found that to achieve the desired effect AMD needed to be concentrated 30x. Even adding AMD at a 30% addition (liquid mass) provided an insufficient amount of sulfate.
Another critical factor is reaction time. Generally, BaSO₄ precipitate forms within minutes, while SrSO₄ takes days [18]. This, however, can limit radium removal, because little time is afforded for inclusion and occlusion to take place, leaving adsorption as the primary co-precipitation mechanism [18]. Furthermore, SrSO₄ is more soluble than BaSO₄, and therefore the potential for Ra²⁺ leaching is greater [38].

Regardless whether radium is co-precipitated with barite or celestite, this research affirmed that “co-precipitation” is a viable method for removing radioactive elements in high ionic strength wastewater. Although similar studies have been conducted, the author is unaware of any which observed such a large disparity between the performance of BaSO₄ and SrSO₄ for radium removal. As noted, there are many unknowns in this study, and it is uncertain whether co-precipitating TENORM as chemical sludge is the best way for the industry to resolve this problem. Ultimately, however, the goal of demonstrating as a lab-scale study that the concentration of radium in this wastewater could be reduced via chemical co-precipitation was successfully met.
A.11 References


APPENDIX B

POWER INPUT TO THE SUPER-CHARGED PULSED JET COMBUSTOR SYSTEM FROM COMPRESSED AIR
In the analysis of the power of the super-charged pulsed jet combustor system discussed in Chapter 6, only the input of fuel was discussed in detail. Utilizing fluid pumps (to push liquid through the system), an electric motor (to turn the air injection valve), and compressed air, however, the true power input to the system was more than just the amount of fuel fed to the combustor. That being said, the power requirements of the chemical metering pumps (0.087 kW each) and the electric motor (¾ HP; 0.6 kW) turning the rotating air-timing valve were known to be so small [1]. Therefore these were not mentioned in Chapter 6, nor will they be discussed further in this appendix. The power required to compress the air necessary for the super-charged pulses of combustion, however, was calculated to determine whether or not it should be included in an overall, thermodynamic system analysis.

The most practical method for calculating the power provided to the system in the form of compressed air was found to be evaluating the power required to charge the tanks at the Penn State University High Pressure Combustion Lab (HPCL), where the system was installed. These two, compressed air storage tanks had a combined total volume of 72 m$^3$ (2,542.66 ft$^3$) and were routinely filled using an ESH, Ingersoll-Rand, 125 HP, industrial air compressor [2]. They were most commonly filled from about 60 psi$_g$ (413.69 kPa) to 120 psi$_g$ (827.37 kPa) using ambient temperature, atmospheric pressure air.

<table>
<thead>
<tr>
<th>Date</th>
<th>T (°F)</th>
<th>RH (%)</th>
<th>BP (in Hg)</th>
<th>DP (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/14/2014</td>
<td>69.8</td>
<td>78</td>
<td>30.04</td>
<td>62.6</td>
</tr>
<tr>
<td>10/21/2014</td>
<td>55.4</td>
<td>77</td>
<td>29.85</td>
<td>48.2</td>
</tr>
<tr>
<td>10/28/2014</td>
<td>73.4</td>
<td>50</td>
<td>29.93</td>
<td>53.6</td>
</tr>
</tbody>
</table>

Table B.1 Meteorological conditions on the dates and at the times of air compression at the HPCL.
their pressure with time
was recorded, as shown in
Figure B.1. Although
meteorological conditions
did vary across the three
dates, as shown in Table
B.1, the rate of pressure
increase within the tanks
remained relatively
constant.

The average rate of tank pressure increase \( y \) (psi) per minute \( x \) could be described by
the linear equation \( y = 1.863x + 60 \). According to this equation, the pressure of both tanks could
be simultaneously raised by 60 psi (413.69 kPa) in 32.21 minutes. The 125 HP power rating of
the GE motor powering the ESH air compressor is equal to 93.19 kW (5,591.4 kJ/min). Thus,
increasing the pressure in these two tanks by
60 psi requires 180 MJ.

Having calculated the potential energy
of the air within the tanks, if the flow rate to
the combustor is known, a compressed air
power to the super-charged pulsed jet
combustor can be found. In general, for all tests, air flow to the combustor was 23 SCFM as read
on the King Instruments Company, Inc. (Garden Grove, CA), 7510216A03, 1FNPT PVC EP 60
SCFM flowmeter. A pressure gauge in the air line immediately after the acrylic air flow meter

\[ ACFM = \frac{14.7 \times (T + 460)}{SCFM \times (P + 14.7) \times 530} \]

Equation B.1 An empirical equation giving
actual cubic feet per minute (ACFM) of air
flow from air flow in standard cubic feet
per minute (SFCM), where \( T \) is air
temperature (in °F), and \( P \) is operating,
gauge pressure (in psi) [3].
usually read 20 psi. According to King Instruments Company, Equation B.1 relates the air flow in SCFM at STP\textsuperscript{54} to actual cubic feet per minute (ACFM) [2]. Using this equation, an air volumetric flow rate of 9.7 ACFM is found.

Using Boyle’s Law ($P_1V_1 = P_2V_2$), if the 2,542.66 ft\textsuperscript{3} tanks are at 120 psi\textsubscript{g}, then, neglecting losses, 5,085.32 ft\textsuperscript{3} of air are available at 60 psi\textsubscript{g}. If the actual flow rate of compressed air is 9.7 cfm, then compressed air could flow to the combustor for just over 520 minutes. Dividing the energy required to compress this air by the total yielded runtime gives 5.8 kJ/s (5.8 kW).

As discussed in Chapter 6, there were two key reasons for not including the power from the compressed air in the overall, system analysis. First, 5.6 kilowatts represents about 9\% the typical, fuel energy input (\textit{i.e.}, about 60 kW). Second, because most other combustors are not of a super-charged nature, including the power required compress air in every calculation, discussion, and table in Chapter 6 would have been tedious and perhaps confusing for the reader.

There was also a third reason this information was put into an appendix and not the body of the thesis. Although it is important to demonstrate that the researchers recognized that power entered the system in the form of compressed air, during experiments detailed notes were not kept regarding any variations in air flow meter readings or changes in the pressure in the air supply line. Therefore, the mass flow rate of compressed air was, theoretically, equivalent for all experiments conducted in Chapters 5, 6, and 7. Consequently, as a relative comparison across all experiments, the addition of seven kilowatts would not change the overall outcome. For example, percent efficiencies of experiments would decrease, but they would all decrease

\textsuperscript{54} STP = Standard temperature and pressure; 20 °C (293.15 K, 68 °F); absolute pressure of 101.325 kPa (14.696 psi, 1 atm).
uniformly. For these reasons, the power added to the system through compressed air was not discussed within the body of the thesis.

APPENDIX B REFERENCES


APPENDIX C

PROPERTIES AND INDUSTRIAL PRODUCTION POSSIBILITIES OF A LOW-EMISSION HYBRID CORE SAND BINDER FOR FERROUS METALCASTING FOUNDRIES
Abstract

Metalcasting facilities in the United States face the daunting task of complying with strict domestic environmental regulations while remaining cost-competitive with overseas markets. One method which foundries can employ is to reduce air emissions before they are produced. A significant contribution to metalcasting emissions are the phenolic urethane core sand binders favored by the industry for their high production, low-scrap performance. Although metal casting producers are reticent to replace their petrochemical core sand binders, if a viable, low-emission core sand binder can be proven to yield equally good results, they might consider the emission reductions to be worth the retooling costs. Working as part of a broader foundry emissions reduction team, a team of environmental engineers at the Pennsylvania State University developed a novel, low-emission, two-part core sand binder. By combining two binder systems already in use by the industry (i.e., collagen and sodium silicate), many of the weaknesses of the individual binders, which prevented them from fully replacing petrochemical binders, were overcome. The work related herein is the continuation of research initiated by the Penn State team to demonstrate the properties of the clean, hybrid core sand binder system (sometimes called X-Link). Specifically, in this work, the author investigated core shakeout, humidity resistance, and automated core production. As expected, the shakeout characteristics of cores made with the hybrid binder system were equal to that of conventional phenolic urethane bonded cores, due to the inclusion of the collagen. In respect to binder humidity resistance and automated core production, however, the performance of the novel hybrid binder system was acceptable only under very specific conditions. Further refinement is required to launch this low-emission core sand binder into foundries across America.
Table of Contents

Units and Nomenclature........................................................................................................... 234
Acronyms.................................................................................................................................. 234
List of Figures............................................................................................................................. 235
List of Tables.............................................................................................................................. 238
Acknowledgements..................................................................................................................... 239
Chapter 1 Introduction............................................................................................................... 240
  1.1 Metalcasting Introduction................................................................................................. 240
  1.2 Importance of U.S. Metalcasting...................................................................................... 240
  1.3 U.S. Metalcasting Challenges.......................................................................................... 242
  1.4 Metalcasting Cores........................................................................................................... 246
  1.5 PSU’s Hybrid Binder......................................................................................................... 249
     1.5.1 Collagen as a Core Sand Binder................................................................................ 249
     1.5.2 Sodium Silicate as a Core Sand Binder..................................................................... 251
  1.6 Hypotheses....................................................................................................................... 252
  1.7 Scope of Work.................................................................................................................. 254
Chapter 2 Core Shakeout........................................................................................................... 255
  2.1 Core Shakeout and UCS................................................................................................. 255
  2.2 Materials........................................................................................................................ 257
      2.2.1 Sodium Silicate.......................................................................................................... 257
      2.2.2 Collagen.................................................................................................................... 258
      2.2.3 Phenolic Urethane................................................................................................... 258
      2.2.4 Mold/Core Box.......................................................................................................... 259
      2.2.5 Oven........................................................................................................................ 259
      2.2.6 Universal Sand Strength Machine.......................................................................... 259
      2.2.7 Sand........................................................................................................................ 259
  2.3 Experimental UCS Methods............................................................................................. 259
  2.4 UCS Results and Discussion............................................................................................ 263
      2.4.1 Phenolic Urethane Core Binder UCS Performance.................................................. 263
      2.4.2 Collagen Core Binder UCS Performance................................................................. 263
      2.4.3 Sodium Silicate Core Binder UCS Performance....................................................... 265
      2.4.4 Hybrid Core Binder UCS Performance................................................................... 268
  2.5 UCS Results Summary..................................................................................................... 269
Chapter 3 HMAC “Part 239” Automated Core Production & Casting Trial.......................... 270
Chapter 4 Core Humidity Resistance....................................................................................... 274
  4.1 Introduction....................................................................................................................... 274
  4.2 Materials........................................................................................................................ 275
      4.2.1 Core Sand Binders...................................................................................................... 275
      4.2.2 Mold.......................................................................................................................... 275
      4.2.3 Oven........................................................................................................................ 276
      4.2.4 Dessicator.................................................................................................................. 276
      4.2.5 Surface Scratch Hardness Testing............................................................................. 277
      4.2.6 Sand........................................................................................................................ 278
  4.3 Method.............................................................................................................................. 278
  4.4 Results............................................................................................................................. 279
Units and Nomenclature

AMP  ampere
cm  centimeters
g  grams
HP  horse power
in  inches ("
lb_f  pounds, force
lb  pounds, weight
mm  millimeters
Pa  pascal (Newton per square meter)
psi  pounds (force) per square inch
SCFM  standard cubic feet per minute
VAC  volts, alternating current
W  Watt

Acronyms

AFS  American Foundry Society
CAAAA  Clean Air Act Amendments
CERP  Casting Emissions Reduction Program
DIMA, DMIPA  dimethyl isopropyl amine
DMEA  dimethyl ethyl amine
DMPA  dimethyl propyl amine
EPA  Environmental Protection Agency (United States)
FAME  Factory for Advanced Manufacturing Education
GDP  gross domestic product
HAP  hazardous air pollutant
HMAC  Hitachi Metals Automotive Components
INC  incorporated
LLC  limited liability company
MACT  maximum achievable control technology
MC  moisture content
MSDS  material safety data sheet
POM  polycyclic organic materials
PSU  Penn State University
PUCB  phenolic urethane cold box
PUNB  phenolic urethane no bake
RCRA  Resource Conservation and Recovery Act
RH  relative humidity
TEA  triethylamine
THC  total hydrocarbon
TRI  Toxics Release Inventory
UCS  unconfined compressive strength
VOC  volatile organic compound
List of Figures

Figure 1.1  Anticipated total 2014 sales forecast for U.S. metal casting markets..............240
Figure 1.2  Global production of gray and ductile iron by the world’s top five iron casting producers.................................................................241
Figure 1.3  The three left-handed amino acid chain helices which make up the right-handed coil of the collagen molecule subunit: tropocollagen.................................250
Figure 2.1  A brick-shaped sand core made with phenolic urethane binder, and heated at 1,000°C (1,832°F) for several minutes; (a) shows the brick exterior – where white silica sand with no remaining binder and black, charred binder can be seen; (b) internal color gradient shows the heat’s penetration and effects...........256
Figure 2.2  The copper mold; (a) shows the individual mold pieces; and (b) shows complete assembly.................................................................260
Figure 2.3  The copper mold broken apart; (a) shows the small cylindrical sand core still in one of the mold halves; and in (b) it is completely removed......................261
Figure 2.4  Small cylindrical cores in the furnace after one hour of thermal treatment. These have been completely degraded by the heat treatment, giving them a default unconfined compressive strength (UCS) of zero..................262
Figure 2.5  Unconfined compressive strength (UCS) of cylindrical cores made with 1.03% (wet mass) commercial phenolic urethane binder. Samples were raised to the indicated temperature for one hour, allowed to cool, then loaded to failure. Unless otherwise noted, all data points represent a sample size (n) of 24. Error bars represent one standard deviation.............................................264
Figure 2.6  Unconfined compressive strength (UCS) of cylindrical cores made with 3.0% (wet mass) hydrolyzed collagen. The samples were raised to the indicated temperature for one hour, allowed to cool, then loaded to failure. Unless otherwise noted, all data points represent a sample size (n) of 24. Error bars represent one standard deviation.............................................264
Figure 2.7  Unconfined compressive strength (UCS) of cylindrical cores made with 3.0% (wet mass) sodium silicate. The samples were raised to the indicated temperature for one hour, allowed to cool, then loaded to failure. Unless otherwise noted, all data points represent a sample size (n) of 24. Error bars represent one standard deviation.............................................265
Figure 2.8  The retained compressive strength of CO2 cured silicate cores after heating to elevated temperatures indicated and cooling to normal temperature. Binder level is not clearly indicated in the source, but is most likely 4.0% .........................266
Figure 2.9  The hot and retained strength of cores using sodium silicate binder. Hot strength refers to soaked at temperature and broken hot, and retained strength refers to soaked at temperature, cooled and broken.........................................................267
Figure 2.10 The tensile and compressive strength after heat treatment of sand cores bound using sodium silicate. The amount of binder added to the sand is not noted....267
Figure 2.11 Unconfined compressive strength (UCS) of cylindrical cores made with 1.75% (wet mass) sodium silicate and 2.0% (wet mass) hydrolyzed collagen binder. The samples were raised to the indicated temperature for one hour, allowed to cool, then loaded to failure. Unless otherwise noted, all data points represent a sample size (n) of 24. Error bars represent one standard deviation..268
The modified, Redford Carver automated core production machine used to produce the “part 249” cores for production trials.

The automated core production process used in Cleveland, OH, to make “part 249” cores with the hybrid binder.

A “part 249” core. The darker color of the sand indicates that this is a “Type 1” core, using lake sand.

Several “part 249” cores. These are “Type 2” cores, using Wedron silica sand.

Castings produced using PSU’s hybrid “part 249” cores; (a) shows a casting after shakeout; and (b) shows a casting after primary shot blasting.

The retired, shell-core, hot box used to produce “part 249” cores for this trial.

A top view of a dog-bone core; (b) the dog-bone mold assembly.

A core and VWR temperature and humidity meter sitting atop a perforated shelf in a desiccator, below which is water.

The Dietert Co. scratch hardness tester which measured relative core surface hardness from 0 to 99; (a) shows the tester in position; (b) the underside of the tester; and (c) the dial read-out.

The relative surface hardness of dog-bone cores made with 1.03% (wet mass) phenolic urethane binder after exposure to low (< 20%) and high (> 90%) relative humidity. Unless otherwise noted, each sample size is three dog-bones, each sampled three times. Error bars represent one standard deviation.

The relative surface hardness of dog-bone cores bindered with 1.75% sodium silicate (wet mass basis) and 2.0% hydrolyzed collagen (wet mass basis) after exposure to low (< 20%) and high (> 90%) relative humidity. Unless otherwise noted, each sample size is three dog-bones, each sampled three times. Error bars represent one standard deviation.

The relative surface hardness of dog-bone cores made with 3.0% (wet mass basis) hydrolyzed collagen after exposure to low (< 20%) and high (> 90%) relative humidity. Unless otherwise noted, each sample size is three dog-bones, each sampled three times. Error bars represent one standard deviation.

The relative surface hardness of dog-bone cores made using 3.0% (wet mass basis) sodium silicate after exposure to low (< 20%) and high (> 90%) relative humidity. Unless otherwise noted, each sample size is three dog-bones, each sampled three times. Error bars represent one standard deviation.

The relative surface hardness of dog-bone cores with (top) 1.0% (wet mass) potassium-lithium silicate added to 2.0% (wet mass) sodium silicate, and (bottom) 1.0% (wet mass) potassium-lithium silicate added to the hybrid binder (1.75% sodium silicate + 2.0% hydrolyzed collagen).

The relative surface hardness of dog-bone cores with 1.75% (dry mass) Fe₂O₃ dry powder added to 1.75% (wet mass) sodium silicate and 2.0% (wet mass) hydrolyzed collagen binders, after exposure to low (< 20%) and high (> 90%) relative humidity. Each sample size is three dog-bones, each sampled three times. Error bars represent one standard deviation.

A dog-bone core produced with silica sand, ferric oxide, sodium silicate hydrate, and denatured collagen.
Figure 5.1  A “part 234” shell core. Notice the much simpler core geometry, compared to the “part 249” cores (see Chapter 3). ................................................................. .289
Figure 5.2  The Harrison Machine Co. core machine delivered to PSU in fall 2011 .......... .289
Figure 5.3  The “part 234” core box used by PSU; (A) through-box vent locations; (B) locations for electric-rod heating elements; (C) core cavity; (D) scratch vents... .290
Figure 5.4  The TinkerOmega MM100 batch mixer ............................................................... .290
Figure 5.5  The FNI Superheat system control box, uninstalled........................................ .291
Figure 5.6  The air heater element. Part of the FNI Superheat System used at PSU........... .291
Figure 5.7  The automated core production process, using the Harrison core machine at PSU ................................................................. .292
List of Tables

Table 1.1  U.S. castings imports as a percentage of total domestic demand............................ 242
Table 1.2  Summarized core sand binder hazardous air pollutant (HAP) emissions...............243
Table 1.3  Primary HAPs of concern for particular foundry coremaking processes and
           binder types............................................................................................................ 244
Table 1.4  Binder systems used to make cores................................................................. 247
Table 4.1  The range of typical surface scratch hardness readings for various core types.....277
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Chapter 1 Introduction

1.1 Metalcasting Introduction

Metalcasting is the process of creating solid shapes by pouring molten metal into a mold and allowing it to cool. Typically, molds are comprised of silica sand, held together with bentonite clay, coal fines, and water, formed into a particular shape. This is called a “green sand” mold, because the adhesive never fully cures [1]. Typically, the green sand mold has an externally square or rectangular shape, with a central cavity. The cavity’s inverse shape gives form to the final, metal casting. Frequently, complex metal castings have intricate external geometry or an internal cavity (e.g., a cylinder within an engine block). To create such castings, separate sand cores are used.

1.2 Importance of U.S. Metalcasting

According to the American Foundry Society’s Modern Casting publication, the United States is the world’s second largest metal castings producer, following China [2]. In 2012, U.S. metalcasting output totaled 12.8 million metric tons –

Figure 1.1 Anticipated total 2014 sales forecast for U.S. metal casting markets [3].
almost 13% of the total world production [2]. Rebounding from the recent recession, the U.S. metalcasting industry has been steadily growing, and by 2015 is expected to reach $37.5 billion in sales [3]. At the current rate of U.S. gross domestic product (GDP) growth, this could be 0.2% of the 2015 U.S. GDP.

As an industry, metalcasting is typically subdivided by iron content in the metal: ferrous (iron and steel) and nonferrous (aluminum, copper, brass etc.). The focus of this paper is on ferrous metalcasting – more specifically, ductile and gray iron. In 2014 U.S. ductile and gray iron sales represented $12.12 billion total sales, as shown in Figure 1.1. In 2012, these two categories accounted for 71% of the world’s cast metal production, with continual growth [2, 3]. In 2012, China led in global gray and ductile iron production, with the U.S. coming in second place for ductile iron, and India the second largest gray iron producer, as shown in Figure 1.2.

Overall, metalcasting is a major U.S. industry. At least 90 percent of all manufactured products contain cast metal components [4]. These cast metal products can be found in just about every economic sector; however, Americans most commonly encounter these in their automobiles [5].
1.3 U.S. Metalcasting Challenges

Although U.S. metalcasting production remains high, metal casting imports are also high (see Table 1.1), with most coming from China, Canada, and Mexico [6]. A 2007 American Foundry Society (AFS) estimate put the rate of U.S. metalcasting industry erosion at 5% annually, and a 2004 report stated that more than 25% of American metalcasting facilities (i.e., foundries) in existence in 1986 have closed [7, 8].

Many factors make foreign metal casting imports economically competitive in the United States. Chief among these are the minimal environmental regulations in many foreign countries [9]. In contrast, U.S. foundries face a staggering number of federal, state, and local environmental regulations and requirements that add to the cost of domestically produced castings. Key among these are the 1990 Clean Air Act Amendments (CAAA) and the US Environmental Protection Agency’s (EPA’s) Toxics Release Inventory (TRI). The 1976 Resource Conservation and Recovery Act (RCRA) gives teeth to these and similar regulations by holding hazardous waste generators responsible for the final disposition of toxic substances through the famous “cradle to grave” system [9]. Environmental compliance costs U.S. foundries millions of dollars annually, causing many metal manufacturers to relocate outside of the U.S. [8, 11].

Although the U.S. metalcasting industry continues to grow, the number of U.S. facilities have dropped by almost 9% since 2009 [3]. With fewer foundry numbers but increasing foundry

<table>
<thead>
<tr>
<th>Year</th>
<th>Castings Import</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997</td>
<td>7%</td>
</tr>
<tr>
<td>2004</td>
<td>18%</td>
</tr>
<tr>
<td>2007</td>
<td>21%</td>
</tr>
<tr>
<td>2008</td>
<td>24%</td>
</tr>
<tr>
<td>2009</td>
<td>23%</td>
</tr>
<tr>
<td>2010</td>
<td>23%</td>
</tr>
<tr>
<td>2011</td>
<td>23%</td>
</tr>
<tr>
<td>2012</td>
<td>22%</td>
</tr>
</tbody>
</table>
output, it comes as no surprise that U.S. foundries are second only to Germany in terms of tons produced per plant, world-wide [2]. To increase output and molding productivity, most ferrous foundries use phenolic, resin-based, petrochemical binders for cores. These organic adhesives have been credited for increasing individual foundry output, especially in the United States [1]. The most commonly used core production methods use tertiary amine catalysts to drive polyurethane-diisocyanate solidification reactions, binding sand grains together in cold-box or no-bake processes (so called because no thermal energy is required to cure the cores) [1, 12]. Sand cores produced in the phenolic urethane cold box process are recognized as being capable of extremely precise, accurate geometries (± 1 mm [0.04 in]) [13]. Trinowski estimated that in the 2007-2008 timeframe, over 125,000 metric tons of phenolic and furan based sand core binders were used in the United States [1].

Although the phenolic cold box and no bake core sand binder systems are highly productive, they generate high emission levels, as shown in Table 1.2 [1]. The primary emission sources are binder thermal decomposition during the molten metal pour, and during mold cooling and shakeout; and solvent evaporation during core production, curing, and storage [1]. As shown in Table 1.3, most of the volatile organic compounds (VOCs) emitted by these and similar conventional foundry core sand adhesives are classified as hazardous air pollutants (HAPs) under the Clean Air Act (e.g., benzene, formaldehyde,

<table>
<thead>
<tr>
<th>Binder Process</th>
<th>lb HAP released per ton metal poured</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUNB&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.520</td>
</tr>
<tr>
<td>Inorganic&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.030</td>
</tr>
<tr>
<td>GMBOND&lt;sup&gt;®c&lt;/sup&gt;</td>
<td>0.073</td>
</tr>
</tbody>
</table>

<sup>a</sup> Phenolic urethane, no bake<br>
<sup>b</sup> Commercial silicate binder<br>
<sup>c</sup> Natural, protein-based binder
methylene diphenyl diisocyanate, phenol, methanol, toluene, etc.) [9]. Of these, free formaldehyde levels are a main concern in the U.S. for phenolic and furan resin binders [1, 8].

When considering the air emissions of the metalcasting industry, regulating agencies do not distinguish the sources of the emissions. Rather, they consider overall output. The EPA has identified 190 chemical compounds as hazardous air pollutants [14]. Forty-five of these have been identified as being “of interest” to metalcasting foundries [8]. According to the EPA’s 2012 TRI report, the “primary metals” industry sector accounts for 10% of the nation’s total industrial sector toxic chemical disposal/release [15]. Further, release by this industry increased by 31% from 2009 to 2012 – up by 4% from 2011 to 2012 alone. This stands in contrast to the national 2011-2012 toxic chemical release decrease of 12% [16].

According to the AFS, out of the 15 identified processes which emit regulated chemical compounds in ferrous foundries, at least eight include cores in some way [17].

Wastes include,

<table>
<thead>
<tr>
<th>System</th>
<th>Binder Type</th>
<th>Pollutant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hotbox/Warmbox</td>
<td>Phenolic Resin-Coated Sand</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol</td>
</tr>
<tr>
<td>Shell</td>
<td></td>
<td>Methanol</td>
</tr>
<tr>
<td>No-bake</td>
<td>Furan/Acid</td>
<td>Benzene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methanol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td>Phenolic/Acid</td>
<td>Formaldehyde</td>
<td>Phenol</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>Toluene</td>
</tr>
<tr>
<td>Phenolic/Ester</td>
<td>Formaldehyde</td>
<td>Phenol</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>Phenol</td>
</tr>
<tr>
<td>Phenolic/Urethane</td>
<td>Formaldehyde</td>
<td>Methylene diphenyl diisocyanate</td>
</tr>
<tr>
<td>Coldbox</td>
<td>Phenolic Urethane</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methylene diphenyl diisocyanate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trieythylene</td>
</tr>
<tr>
<td>Phenolic/Ester</td>
<td>Formaldehyde</td>
<td>Phenol</td>
</tr>
</tbody>
</table>

55 Primary metals refers to industrial facilities which produce metal products from ore, pig, or scrap [18].
“particulates of sand and other refractory materials, spent sand; damaged cores; organic compounds; HAPs; VOCs; carbon monoxide; hydrogen sulfide; sulfur dioxide; nitrous oxide; metallic oxide fumes; ammonia; hydrogen cyanide; nitrogen oxides; polystyrene vapors; wastewater with suspended solids, phenols, dissolved salts, and elevated temperature” [9]. The predominant source of air emissions in ferrous foundries is the use of organic chemical, core sand adhesives called “binders” – specifically phenolic resins and furans [9]. Gaseous chemical emissions occur during core mixing, production, storage, the molten metal pour, cooling, and shakeout. Of the core processes prior to placement in the pour, core production has been found to release the most VOCs, and polycyclic organic materials (POMs), many of which are HAPs [19].

Per the Clean Air Act and its most recent 1990 Amendments, the US EPA must regulate industrial “major sources” of HAPs [1]. Consequently, foundries must accurately report and predict their hazardous air emissions. Doing so, however, is difficult. Overestimating results in unnecessary regulatory compliance cost; underestimating, however, could result in a violation and a hefty fine. Consequently, to build a highly accurate database to enable more precise foundry emissions estimates, in 1994 the Casting Emissions Reduction Program (CERP) was established [8]. CERP continued for 14 years, providing the most comprehensive air emissions profile of metalcasting molding and casting process [1].

Presently, U.S. production industries must meet maximum achievable control technology (MACT) standards. To be compliant, foundries traditionally rely on conventional, air pollution-control technologies like scrubbers, cyclones, baghouses, and electrostatic precipitators [1, 9, 20, 21]. Typically, these existing systems are upgraded, at great financial cost [22]. It is preferable,
however, to avoid generating VOC and HAP emissions, rather than trying to capture and remove them after they are created.

The U.S. metalcasting industry recognizes the need for a cleaner core sand binder. In 2002, the Cast Metals Coalition (CMC; a partnership between the AFS, the Steel Founder's Society of America, and the North American Die Casting Association) published an industry vision document. According to the CMC, scrap and production cost reduction, along with improved product performance through waste management are key 2020 industrial goals [5]. The development of “more environmentally sound [core sand] binders” is mentioned as critical to meeting these objectives. Provided they can offer physical and mechanical properties equivalent to current petrochemical binders, U.S. foundries would welcome replacement, lower emission sand binders [23].

1.4 Metalcasting Cores

Sand cores are critical to most metalcastings. As previously noted, a core is predominantly sand (or a similar, inert aggregate) held together by a small amount of binder [24, 25]. Cores form internal cavities or produce particularly intricate surface shapes in metal castings [26]. According to Dietert, a core must meet many stringent and often conflicting requirements. For example, “A core must be strong enough in the process of preparation to retain its form without deformation. After...drying, it must be sufficiently strong to resist erosion and deformation by metal during the filling of the mold. ... It must have a minimum of contraction and expansion. ... It must have sufficiently low residual gas forming materials to prevent excess gas from entering the metal, and the metal must remain quiet in contact with the core during pouring and solidification. On the other hand, the core must disintegrate, following
initial [metal] solidification, to minimize strains on the casting and to make its removal from the casting easy during shaking out” [26]. A simpler definition for a “good” core would be, “The ability to produce quality castings with minimal scrap” [27].

High volume cores are produced by automated machines, called core “blowers” or “shooters” [1]. In these, sand which has been pre-coated with resin or a sand and binder mixture are conveyed to a small hopper. For a sand-binder mixture, the time between mixing completion and creating a hard core by blowing or compaction is called “work time” or “bench life,” and is typically minutes long, though it can be lengthened by adding “inhibitors” or “extenders” to the binder [1, 28]. Work time is critical for water-based binder systems (e.g., denatured proteins, alkali-silicates, etc.) because water evaporation causes premature sand hardening, hampering core production and reducing core strength. Also, once a core has been produced, it should have a good storage or shelf life, able to retain its overall strength and good surface properties for days before use [24].

The prepared sand and binder are blown under pressure into two joined mold halves. This mold is called the “core box,” and it gives shape to the compacted sand mixture. Physical and

<table>
<thead>
<tr>
<th>Binder System</th>
<th>Cure Method</th>
<th>Typical Binders Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hotbox or Shell</td>
<td>Heat</td>
<td>Phenolic resins, Furan resins, Phenolic/furan resins, Urea modified resins</td>
</tr>
<tr>
<td>Warmbox</td>
<td>Heat</td>
<td>Phenolic resins, Furan resins, Urea modified resins</td>
</tr>
<tr>
<td>Nobake</td>
<td>Acid, Ester</td>
<td>Furan, Phenolic, Phenolic, Phenolic urethane, Alkyd urethane</td>
</tr>
<tr>
<td>Coldbox</td>
<td>Amine, Ester</td>
<td>CO₂ gas</td>
</tr>
</tbody>
</table>
chemical conditions within the box are carefully maintained to promote the rapid curing of the bonds within. Once the core is sufficiently cured, the core box parts (vertically or horizontally, depending on design) and a solid core is removed and stored for future use.

Core hardening is achieved by the addition of heat and/or the application of a liquid or gas catalyst. The cure method dictates what type of chemical binder will be used and the curing sequence (see Table 1.4). Generally, thermal core hardening is used in hot box, shell, and warm box core production. Warm box temperatures range from 300 to 450°F (150-230°C), while the typical hot box or shell temperature range is 450 to 600°F (230-316°C) [9]. Hot box and shell techniques literally melt together the phenolic or furan resins which coat the sand grains. No-bake and cold box techniques rely on gases (typically CO₂, or an amine, ester, or acid) to harden the core at room temperatures [9].

Although core properties are aggregate-dependent, the binder most influences the core properties. Presently, phenolic urethane is the industry standard and benchmark core sand binder [12]. This binder system is typically used in a cold box (phenolic urethane cold box [PUCB]) processes or no bake (phenolic urethane no bake [PUNB]) process, where a tertiary amine catalyzes the reaction between phenolic resin and polyisocyanate. The difference between no bake and cold box is the form of the amine catalyst – liquid versus gas atomized, respectively [29]. Tertiary amines used include triethylamine (TEA), dimethyl ethyl amine (DMEA), dimethyl isopropyl amine (DMIA or DMIPA), and dimethyl propyl amine (DMPA) [1, 25, 28]. Because of its insensitivity to sand type, high tensile strength, and ability to produce dimensionally-accurate cores, the PUNB/PUCB processes have replaced shell (croning) core production as the widely used core production process world-wide [1, 30].
1.5 PSU’s Hybrid Binder

During his time at Penn State University (PSU), Fox developed a hybrid, low-emission, foundry core sand binder system (sometimes called X-Link). The two-part formulation used denatured, hydrolyzed collagen and a commercial, sodium silicate binder. To a limited extent, ferrous foundries used both products, but only as stand-alone binders. After rigorous testing to identify suitable collagen crosslinkers, Fox identified the synergistic sodium silicate and collagen combinations that most closely matched the performance of phenolic urethane.

1.5.1 Collagen as a Core Sand Binder

Historically, “proteins” have been used as a foundry core sand binder. In his 1966 book Foundry Core Practice, Harry Dietert lists the benefits of protein binders (i.e., organic compounds containing nitrogen, as gelatin, casein and glue) as: high collapsibility, high binding power, rapid drying, improved sand flowability, fair moisture resistance, and mild gas evolution [26]. This “mild gas evolution” is synonymous with “low VOC emissions.”

A specific protein binder which has emerged as a promising, low-VOC foundry core sand binder is collagen. In a 1954 Nature article, two Indian physicists, Ramachandran and Kartha, quantified collagen as a triple helical polypeptide structure (see Figure 1.3) [31]. This triple helical structure is thermally stable and mechanically strong, yet its hydrogen bonds can be readily denatured in water above 62°C and can cross-link or react with other molecules [32, 33]. Furthermore, collagen’s denature is fully reversible. When a denatured collagen solution dehydrates, the linear, amino acid chains randomly re-bond, via hydrogen bonding [34]. Although, compared to covalent bonding, hydrogen bonds are relatively weak, their sheer number can impart a high level of adhesive strength.
Collagen is a particularly attractive adhesive because it is readily available and inexpensive. Being the most abundant protein in animals, meat processing waste is high in collagen content [32, 35]. Consequently, dried, shredded collagen can be obtained from the food processing industry as a waste.

For the research herein, collagen was obtained from Entelechy, Inc. (Plymouth, MI). The original source was Hormel Foods Corporation (Austin, MN), which markets it as GMBOND® core sand binder [36]. According to its MSDS, GMBOND® is >99.5% amino acids (“protein product”), with insignificant amounts of iron oxide, methyl paraben, propyl paraben, benzalkonium chloride, and sodium benzoate. Overall, it is about 50% carbon, 25% oxygen, and 17% nitrogen [37]. As its name implies, GMBOND® was developed by General Motors in the 1990s. In 1994, however, the company abandoned it, and five years later Hormel Foods Corporation received sole product licensing rights to GMBOND® [1, 38, 39].

Although a promising adhesive, collagen’s weak hydrogen bonds cannot withstand the high temperatures from molten metal contacted with the mold, causing core erosion during pouring and subsequently causing casting defects [23]. Conversely, a core binder must lose its strength for easy shakeout of the casting after cooling, making weak hydrogen bonds (and organic binders, in general) an attractive feature. Consequently, for those in the foundry industry seeking an organic, low-VOC binder, phenolic urethane replacement, collagen is a viable option.

Trinowski praises collagen,

Figure 1.3 The three left-handed amino acid chain helices which make up the right-handed coil of the collagen molecule subunit: tropocollagen [40].
stating that collagen has “the lowest emissions of any organic foundry binder” [1]. It has proven that cores produced with collagen binder generate about $\frac{1}{10}$th the VOC emissions of similar cores made using the PUCB process, and collagen also has excellent shakeout characteristics [12, 38, 39].

1.5.2 Sodium Silicate as a Core Sand Binder

For over 50 years, the American foundry industry has used hydrated sodium silicate (also known as “water glass”) as a core binder [41-43]. England in 1898 is its first recorded use [26]. Producing cores with sodium silicate is considered simple, and the binder can yield highly accurate core geometries [26]. Many alkali silicates can be used as core sand binders; however, due to its low cost, of these sodium silicate is the most commonly used [43].

Sodium silicate core binders can be cured by applying inorganic salts, organic or mineral acids, inorganic oxides, or thermal energy [43]. The most common core curing method is CO$_2$ gassing. Proposed chemical reaction equations for the hardening of sodium silicate via carbon dioxide gas are $\text{Na}_2\text{SiO}_3 \cdot x\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{SiO}_2 + \text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ or $\text{Na}_2\text{Si}_2\text{O}_5 \cdot \text{H}_2\text{O (l)} + \text{CO}_2 (g) \rightarrow \text{SiO}_2 (gel) + \text{Na}_2\text{CO}_3\text{H}_2\text{O (glass)}$ [24, 26]. In both cases, the reaction product is a hydrated sodium carbonate. Sodium carbonate is a primary ingredient in glass production [44].

Sodium silicate’s most significant advantage as a foundry core sand binder is its low VOC emissions – three orders of magnitude less than PUNB [1, 45]. The construction industry also uses sodium silicate in fire protective coatings on structural members due to its low VOC generation [46].

Unfortunately, cores produced using sodium silicate binders have poor collapsibility and shakeout properties [26, 28, 45]. Under the molten pour’s extreme temperatures, the gelatinous
sodium carbonate bonds become glass, permanently fusing sand grains together, thus preventing easy shakeout. Additionally, sodium silicate absorbs ambient moisture, which breaks chemical bonds, thus degrading core strength and surface properties which dramatically limits core storage life [24, 28, 45, 46]. Sand grains bonded together using sodium silicate also have a limited re-use life, as glass accumulates on grain surfaces, hindering future re-bonding [1].

For the research herein, a modified, hydrate sodium silicate solution (Cast Clean®) was provided by J.B. DeVenne, Inc. (Berea, OH). A proprietary mixture, this solution contained additives to enhance core collapsibility, improve moisture resistance, and decrease glass buildup on sand grains. When completely dehydrated, it was found to be 41.3-42.5% by mass of dry solids, which is in agreement with the recognized industry standard for sodium silicate binders [27, 28, 43, 47]. For ferrous casting, cores usually employing sodium silicate binder at 3.0-3.5% (wet mass), and the binder’s SiO₂ to Na₂O (silica to soda) ratio is typically between 3:1 and 2:1 [28].

1.6 Hypotheses

As previously discussed, sand cores are critical to metalcasting. A successful core must simultaneously meet many paradoxical requirements. Fully evaluating a core binder’s effectiveness requires full-scale automated production, and comprehensive casting trials. These, however, are expensive and labor-intensive endeavors. Alternatively, a core binder’s properties may be assessed through laboratory-scale experiments.

When the author began this work, Fox – in pursuance of his Ph.D. – had already investigated the tensile strength, hot distortion, and erosion properties of the hybrid binder system, and all were considered favorable [47]. A full-scale casting study, however, had not yet
been completed. Consequently, the author began investigating the binder’s shakeout properties, since this was a key core performance measure.

During an initial short-run casting trial, the author and Fox produced over 200 cores using the hybrid binder system. These cores were used in a full-scale casting trial at the Hitachi Metals Automotive Components (HMAC) foundry in Lawrenceville, PA. The cores were manufactured at a collaborator’s facility in Cleveland, OH, and subsequently transported to State College, PA, for storage prior to being moved to Lawrenceville for the casting trial. This work revealed two key weaknesses of the hybrid binder system: (1) core production was challenging and relied heavily on core box condition and venting; and (2) humidity degraded cores produced with the novel, two-part binder system [47].

In the fall of 2011, an automated, Harrison Machine Company core machine was installed in PSU’s FAME laboratory. Using this machine, the author began investigating the production properties, methods, and best practices for full-scale core production using the hybrid binder system. The goal was to produce over 2,000 “good” cores for a second, more extensive casting trial at HMAC’s Lawrenceville, PA, facility during the fall of 2012. HMAC would use the cores on their production line, while a stack test, monitoring real-time air emissions was conducted.

All the aforementioned issues can be neatly surmised by the following research hypotheses:

1. The hybrid, low-emission, core binder system developed at PSU will possess excellent shakeout characteristics, during cast iron production trials.
2. The sodium silicate binder portion of hybrid system is hygroscopic, causing it to absorb ambient moisture during storage, thus decreasing core surface properties leading to sand-related defects in the metal castings produced using these cores.

3. The sand cores produced with the hybrid binder system can be successfully manufactured using an automated core machine, using core blowing parameters similar to those already used in industrial, foundry production.

1.7 Scope of Work

The ultimate purpose of this work was the industrial acceptance of the PSU hybrid binder system by iron foundries across America. The author began working on the project in the spring of 2011. Several military training interruptions, followed by an eventual deployment to Afghanistan, however, prevented him from completing the work. In the author’s wake, Joshua Allen continued and ultimately finished the project.

This work is included as appendix to the author’s primary M.S. thesis. It is divided into six chapters. Chapter 1 is the introduction, and Chapter 6 is the conclusion. Chapter 7 contains the references cited within this appendix. The author’s research is covered in the chapters between.
Chapter 2 Core Shakeout

2.1 Core Sand Shakeout and UCS

The material requirements imposed on foundry sand cores are paradoxical. Initially cores must withstand handling, storage, and contact with molten metal often at temperatures above 1,500°C (2,732°F) [23]. Less than an hour later, however, the core sand binder must degrade so that the sand grains can be broken apart with little applied energy. This process casting-mold separation is called shakeout or knockout [26, 48, 49].

The foundry industry employs many shakeout methods. These include vibrating tables, shot-blast units, tumblers, hydraulic jets, pneumatic hammers, and in extreme circumstances: hand-removal [26, 48]. Following pouring, molds cool on a conveyor belt. Once the cooling time has elapsed, the filled molds encounter knockout. Foundries expect the mold and/or core aggregate to readily separate from the metal casting, so that the mold and core material can be processed for reuse [47, 49].

According to Dietert, there are six key factors in core shakeout: the casting design; the core sand type; the core sand binder; the core baking or curing method; the cooling time the casting is in the mold; and the shakeout equipment type employed [26]. The core binder, quantity and type have the greatest impact on core performance [26].

While collagen’s hydrogen bonds are readily thermally degraded, sodium-silicate core sand binders have a poor shakeout performance history [28, 41, 48]. The high temperatures to which the cores are subjected during the casting turns the gelatinous sodium silicate bonds to glass, rather than decomposing them. To address this issue, “modifiers” (*i.e.*, organics or
phosphates) are commonly added to the sodium silicate binder, improving the binder’s knockout performance [41, 48].

A full-scale, casting trial is the best shakeout evaluation method. This is, however, an expensive, labor-intensive endeavor. Consequently, evaluating core binder collapsibility on a laboratory scale is desirable. Laboratory methods to evaluate core binder decomposition, however, are not widely known or practiced.

In 1966, Dietert wrote, “[The compressive strength of a core at room temperature after it has been heated to an elevated temperature in own (sic) atmosphere] is a good laboratory measure for predetermining the core knockout effort of various core mixtures” [26]. Additional literature indicates that this technique (or variations thereof) is commonly used [29, 48, 50, 51]. Thermal gradient within a large core heated to a high temperature is shown in Figure 2.1. Exposed to the solidifying molten metal, a core’s surface will experience the temperatures close to the molten metal temperature. This, however, will dissipate through the core. So while the binder nearest the metal surface may be completely decomposed, the core’s interior may remain hard and relatively unaffected.

Figure 2.1 A brick-shaped sand core made with phenolic urethane binder, and heated at 1,000°C (1,832°F) for several minutes; (a) shows the brick exterior – where white silica sand with no remaining binder and black, charred binder can be seen; (b) internal color gradient shows the heat’s penetration and effects.
To mimic molten metal contact, the author created miniature cores using various core sand binders. These were then thermally treated and their unconfined compressive strength (UCS) – sometimes referred to as “retained strength” in other literature – was measured. Core UCS after thermal treatment was considered indicative of shakeout performance (i.e., lower UCS indicated more favorable shakeout performance).

2.2 Materials

2.2.1 Sodium Silicate

As previously noted, a commercial, hydrated sodium silicate solution (Cast Clean®) provided by J.B. DeVenne, Inc. (Berea, OH) was used in this research. Cast Clean® is presently used in the metal casting industry. It was generally understood that it contains proprietary collapsibility-enhancing additives to improve core shakeout. By dehydrating a liquid sample, Fox found this proprietary sodium silicate foundry binder to be 42.5% solids [47].

When used as a stand-alone binder in this research, a mass of hydrated sodium silicate liquid solution equal to 3.0% of the dry sand’s mass was mixed into the sand. As a component of the hybrid binder system, the sodium silicate hydrate addition was 1.75% (wet) the mass of the dry sand. Reported sodium silicate binder content in sand cores is between 2.5% to 7% – though a 3.0% to 4.0% (wet) mass addition seems most preferred [26, 28, 48]. As with any binder system, however, core binder addition should not exceed the amount required to produce the necessary required strength in the resultant core [48].

56 A less cumbersome explanation for binder addition is to say that the content of sodium silicate hydrate in the sand and binder mixture is 3.0% (wet) mass.
2.2.2 Collagen

Collagen was provided by Entelechy, Inc. (Plymouth, MI). A liquid solution of
denatured, hydrolyzed collagen was created by adding a mass of water equal to twice the mass of
dry collagen to be dissolved. The mixture was denatured in a hot water bath, kept between 70-
80°C (158-176°F). In this work, the collagen addition will be reported on a wet mass basis –
referring to the mass of a hydrolyzed, denatured collagen solution, prepared as stated above.\footnote{This is done for ease of comparison; however, in the CERP studies, for example, the “binder” addition did not consider water to be part of the protein core sand binder system\cite{39}. Therefore, even though adding 1.0% (dry) mass of dry GMBOND\textsuperscript{®} powder required adding a mass of water equal to 2.0% the sand’s mass, binder addition in this scenario was considered to be 1.0%, and equivalent to adding “1.0%” of commercial, phenolic urethane binder.}

When used as a stand-alone binder in this research, it was added to dry sand at a 3.0% (wet)
mass basis. As a component of the hybrid binder, its addition was 2.0% (wet) the sand’s dry
mass. During CERP casting trials using GMBOND\textsuperscript{®} as a stand-alone binder, a similar protocol
was followed, where the dried protein mass was 1.0% (dry) the mass of the sand, and it was
made soluble in a mass of water 2.0% (wet) the mass of the sand\cite{39}.

2.2.3 Phenolic Urethane

Because phenolic urethane core sand binder is considered the industry-standard, PSU
produced comparison core samples using a two-part, liquid mixture: phenolic urethane and ethyl
amine (DMEA)\cite{52}. This is the widely used ISOCURE\textsuperscript{TM} binder system developed by Ashland
Chemical Company (Dublin, OH)\cite{1}. As a substitute for curing using amine gas, heat was used.
Molds filled with the wet sand and binder mixture was placed in a 110°C (230°F) oven for 24
hours to cure. Liquid binder percentage addition was 1.03% of the dry, sand mass, on a wet
mass basis.\footnote{This is a common binder level for phenolic urethane core sand binder systems\cite{25}.}
2.2.4 Mold/Core Box

The mold/core box used to make the small, cylindrical UCS cores was hand-made from 0.5” (1.27 cm) diameter copper piping and fittings. More details are provided below in Section 2.3.

2.2.5 Oven

The cylindrical cores were cured in a VWR® Scientific Model 1305U Utility oven, maintained at 110°C (230°F). They were thermally treated in a Barnstead/Thermolyne 1400 series benchtop muffle furnace.

2.2.6 Universal Sand Strength Machine

A Model 42104, Electronic Universal Sand Strength Machine (Simpson Technologies Corporation, Aurora, IL) assessed the cylindrical cores’ unconfined compressive strength (UCS). According to the manufacturer, the unit’s load cell capacity is 1,102 lb (4,902 N) [53]. The samples were unconstrained during compression.

2.2.7 Sand

The core sand used in these experiments was a foundry grade washed sub angular silica sand from the Wedron Silica Company (Wedron, IL), and had a specified AFS grain fineness number ranging from 67-73.

2.3 Experimental UCS Methods

To make the cylindrical cores, binder was added to 700 grams (1.54 lb) dry, Wedron silica sand batches, and was mixed for one minute using a commercial Kitchen Aid Mixer,
Model Number KSMC50S (St. Joseph, MI) with a flat-beater head. When combining sodium silicate hydrate and hydrolyzed collagen, the sodium silicate solution was always added first, coating the sand grains prior to the collagen addition.

To keep compressive strength manageable, a 0.5 inches (1.27 cm) maximum sample diameter was used. Because the sand testing machine was intended to accommodate traditional 2” tall by 2” diameter (5.08 x 5.08 cm) samples, it was found that longer cylindrical cores best fit the testing machine. If they were too long, however, bending would certainly occur, causing tensile failure – a failure mode which would occur long before compressive failure. Consequently, sample length was kept ≥1” (2.54 cm) but ≤1.5” (3.81 cm) and a metal shim was carefully inserted between the machine’s loading locations and one sample end. Although the author observed compressive failure for all samples, with such a high L/D ratio (2-3) it is likely that some samples failed due to tensile stress.

To create a cylindrical sample, commercial 0.5” (1.27 cm) copper tubing was used. This was cut into 1.75” (4.45 cm) length sections and carefully split axially, creating two halves. These pieces slid snugly into a copper sleeve (about 1” [2.54 cm] long), thus joining the 0.5” (1.27 cm) tubing sections. Figure 2.2 shows the assembled mold and its components.
Once sand and binder were properly mixed, equal mass amounts were measured into plastic weigh boats. The contents of each weigh boat were carefully funneled into an assembled, copper mold. Using a 3/8” (0.95 cm) diameter aluminum rod, the wet core sand and binder was compacted by hand. Filled and compacted molds were placed on a ceramic tile, which was inserted into an oven. The samples thermally cured at 110°C (230°F) in an oven for one hour, and were then removed to cool.

Within about 15-20 minutes after coming out of the oven, the molds were sufficiently cool to be carefully disassembled, removing the cylindrical core within. Figure 2.3 shows a small core inside a disassembled mold, followed by a picture of the entire assembly after the core was removed.

Once the cylindrical sand cores were freed from the mold, their shape was slightly and very carefully adjusted. On a pre-leveled surface, one end of the cylinder was gently abraded until both ends were square (as verified by a small level). Additionally, the geometrically opposing “fins” (created by the mold geometry) which ran down the long axis of the cylinder were gently removed via abrasion, yielding a more uniform shape. Following this step, the cores were stored in a vacuum desiccator (wherein the relative humidity [RH] was maintained at <20%) until tested.

Figure 2.3 The copper mold broken apart; (a) shows the small cylindrical sand core still in one of the mold halves; in (b) it is completely removed.
Samples were thermally treated in a benchtop muffle furnace. The maximum temperature of this furnace was 1,110°C (2,030°F). Cylindrical cores were carefully laid on a ceramic tile, which was inserted into the muffle furnace. Thermal treatment lasted for one hour at the desired temperature.\textsuperscript{59}

Once the samples cooled for one hour following heat treatment, they were carefully transported to a nearby laboratory. There the cylinders were axially loaded to compressive failure using the Electronic Universal Sand Strength Machine. This unit automatically loaded the sample on command, and digitally output the compressive failure load (in lb). Prior to UCS testing, each sample’s diameter was measured so that compressive strength in units of force per cross-sectional area (\textit{i.e.}, psi or kPa) could be determined.

Figure 2.4 shows the condition referred to as 0 kPa/psi, UCS. No UCS after heat treatment implied that the core binder had completely thermally degraded. As shown in Figure 2.4, at this condition the cores completely disintegrated under the influence of gravity.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Small cylindrical cores in the furnace after one hour of thermal treatment. These have been completely degraded by the heat treatment, giving them a default unconfined compressive strength (UCS) of zero.}
\end{figure}

\textsuperscript{59} Initially, thermal treatment in an O\textsubscript{2}-free environment was believed to be important, as it would better simulate the oxygen-deprived conditions within a sand core during and after casting. According to literature, however, during laboratory experiments it is common to thermally treat sand cores in “own” (versus “reduced”) atmosphere [26, 29].
2.4 UCS Results and Discussion

2.4.1 Phenolic Urethane Core Binder UCS Performance

As shown in Figure 2.5, as the thermal treatment temperature increased, the unconfined compressive strength (UCS) of the cylindrical cores produced with 1.03% (wet mass) commercial phenolic urethane binder decreased. Because all the cylindrical cores were thermally cured at 110°C, this was considered the initial heat-treatment condition (i.e., cores were cured at this temperature, but not exposed to it again for one hour, when creating the “110°C” UCS data point). After being exposed to 400°C (752°F) for one hour, these core samples quickly failed under a small compressive load around 345 kPa (50 psi). Considering that phenolic urethane is the industry’s standard and benchmark core sand binder, the results in Figure 2.5 represent good collapsibility and shakeout behavior.

2.4.2 Collagen Core Binder UCS Performance

Figure 2.6 shows the UCS behavior of cylindrical cores made with 3.0% (wet mass) hydrolyzed collagen after thermal treatment. These results closely mimic those of phenolic urethane (see Figure 2.5). After being exposed to 400°C (752°F), these core samples quickly failed under only 230 kPa (33 psi) – 115 kPa (17 psi) less than samples made using phenolic urethane binder, after the same heat treatment condition. This supports the reported and observed positive shakeout performance of GMBOND® and other protein binders.
Figure 2.5 Unconfined compressive strength (UCS) of cylindrical cores made with 1.03% (wet mass) commercial phenolic urethane binder. Samples were raised to the indicated temperature for one hour, allowed to cool, then loaded to failure. Unless otherwise noted, all data points represent a sample size (n) of 24. Error bars represent one standard deviation.

Figure 2.6 Unconfined compressive strength (UCS) of cylindrical cores made with 3.0% (wet mass) hydrolyzed collagen. The samples were raised to the indicated temperature for one hour, allowed to cool, then loaded to failure. Unless otherwise noted, all data points represent a sample size (n) of 24. Error bars represent one standard deviation.
2.4.3 Sodium Silicate Core Binder UCS Performance

Figure 2.7 shows the UCS behavior of cylindrical cores made with 3.0% (wet mass) sodium silicate hydrate after thermal treatment. Although core UCS is low (<690 kPa; 100 psi) between 400-600°C (750-1,110°F), it recovers to over 3,100 kPa (450 psi) by 800°C (1,470°F), and 2,070 kPa (300 psi) at the maximum thermal treatment temperature of 1,110°C (2,012°F).

Work presented by Dietert, Owusu, and Nicholas (see Figures 2.8-2.10), confirms an initial UCS decrease followed by strength rebound as heat treatment intensifies for cores produced using sodium silicate binder. Of these three sources, Owusu best explains this effect using a very detailed, chemistry-based analysis [51]. In particular, Owusu asserts that the minimum strength region in the 450-550°C (842-1,022°F) temperature range is caused by the

![Figure 2.7 Unconfined compressive strength (UCS) of cylindrical cores made with 3.0% (wet mass) sodium silicate. The samples were raised to the indicated temperature for one hour, allowed to cool, then loaded to failure. Unless otherwise noted, all data points represent a sample size (n) of 24. Error bars represent one standard deviation.](image-url)
sodium carbonate gel bonds partially liquefying. At higher temperatures, however, these bonds vitrify, becoming solid glass.

In a 2011 paper, Izdebska-Szanda and Balinski used “residual strength”\(^{60}\) to characterize sodium silicate binder’s “knock out” (i.e., shakeout) properties after heat treatments ranging from ambient temperatures to 900°C (1,652°F) [41]. They also found an initial strength increase, peaking at about 5,200 kPa (754 psi) at 200°C (392°F), dropping to about 400 kPa (58 psi) from 500-700°C (932-1,292°F), and then regaining strength, achieving about 2,400 kPa (348 psi) at 900°C (1,652°F).

Comparing UCS results between tests conducted by different authors is difficult because important experimental details are sparse. For example, core dimensions are critical but often go unreported. Brown states that core compressive strength is typically measured on 50 mm (1.97”) diameter cores using AFS 2” diameter tubes [28]. Briggs, however, states that the standard AFS compression testing geometry is a 1.125” (28.575 mm) diameter by 20 in (50.8 cm) long cylindrical core, heat treated for 12 minutes in a furnace [29].

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\(^{60}\) Although the meaning of “residual strength” is unclear in their 2011 paper, a year later in another paper by Izdebska-Szanda, et al., a similar “residual strength vs. treatment temperature” graph appears, and here “residual strength” clearly refers to “compressive strength” [50].
Another important note is that this study’s sodium silicate binder was a commercial, proprietary product, adjusted for improved shakeout performance. Other authors use commercial alkali silicate binders, but some use a pure sodium silicate solution. For example, Dietert’s data is based on a commercial binder, while it appears Owusu used pure sodium silicate. Furthermore, binder percentage is often unreported. Data presented by Dietert, however, does provide the binder percentage – 5.0%, which significantly exceeds the 3.0% level used in PSU experiments.

Figure 2.9 The hot and retained strength of cores using sodium silicate binder. Hot strength refers to soaked at temperature and broken hot, and retained strength refers to soaked at temperature, cooled and broken [26].

Figure 2.10 The tensile and compressive strength after heat treatment of sand cores bound using sodium silicate. The amount of binder added to the sand is not noted [51].
2.4.4 Hybrid Core Binder UCS Performance

Although collagen and a commercial sodium silicate binder have never been reportedly mixed, the PSU hybrid system imitates the industry practice of enhancing alkali-silicate binder collapsibility by adding organic material (e.g., cereals, oils, etc.) [28]. The organic component both aids in holding the core together during handling and pouring, and may also provide sufficient thermal bond degradation for effective core shakeout.

Figure 2.11 represents the experimental UCS results from experiments conducted using collagen and sodium silicate as a hybrid binder system. Based on these results, it can be concluded that adding collagen to sodium silicate lowers core UCS after thermal treatment. Although UCS never reached zero, it remained below 620 kPa (90 psi) from 600-1,000°C (1,112-1,832°F), which is more than 1,370 kPa (200 psi) below the average UCS of sodium

![Figure 2.11 Unconfined compressive strength (UCS) of cylindrical cores made with 1.75% (wet mass) sodium silicate and 2.0% (wet mass) hydrolyzed collagen binder. The samples were raised to the indicated temperature for one hour, allowed to cool, then loaded to failure. Unless otherwise noted, all data points represent a sample size (n) of 24. Error bars represent one standard deviation.](image-url)
silicate in this temperature range, per the experimental results for 3.0% sodium silicate binder presented in Figure 2.7 above. Therefore, combining collagen and sodium silicate should result in sand cores which readily shakeout following the solidification of a ferrous metal casting.

2.5 UCS Results Summary

Sand core shakeout behavior was investigated by heating small, cylindrical cores to elevated temperatures, allowing them to cool, and then measuring their UCS. The results from these experiments confirmed two important expectations: (1) collagen alone retains about as much strength after heat treatment as phenolic urethane; (2) simultaneously using collagen and sodium silicate binders significantly lowered core UCS after high-temperature exposure. Even a relatively low collagen addition (2.0% [wet] mass) sufficiently reduced grain-to-grain bond strength up to 1,100°C (2,012°F), overcoming the glassification effect of sodium silicate bonds which inhibits core sand shakeout after ferrous casting solidification.
In 2011, the PSU team produced over 200, Hitachi Metals Automotive Components (HMAC) USA, LLC, “part 249” sand cores at a project collaborator’s facility in Cleveland, OH. At this facility, a Redford Carver, cold box, horizontal-part automated core machine had been retrofitted for use with Cast Clean® binder (see Figure 3.1). Modifications included a heated sand magazine, and an electrically heated core box – making the core blower suitable for use with warm box binder systems. Further, a Superheat System (produced by Furness-Newburge, Inc., Versailles, KY) was installed. This system rapidly heated pressurized air, which was blown through the core box, curing the water-based binder via evaporation. This increased cross-linking density and provided higher, immediate out-of-box

Figure 3.1 The modified, Redford Carver automated core production machine used to produce the “part 249” cores for production trials.

Figure 3.2 The automated core production process used in Cleveland, OH, to make “part 249” cores with the hybrid binder.
strengths via accelerated solvent evaporation. Purging core boxes with heated air has been used in the foundry industry, where it is referred to as a “cold box plus” system [1].

Due to a sand shortage, two sand types were used for this trial: lake sand (HMAC’s the conventional sand) comprised “Type 1” cores, while “Type 2” were made from Wedron silica sand (which PSU typically used in lab-scale tests). (Figures 3.3 and 3.4 show the visible color differences between the two core types resulting from the different sand types.) The Type 1 sand was used for 41% of the cores; the remaining 59% were produced with Type 2 sand. For all cases, the hybrid binder was used: hydrolyzed collagen was added to sand at a 1.0% (wet) mass basis, and the sodium silicate mass addition was 1.6% (wet).

These cores were introduced into HMAC’s molding line during standard production. They were placed into flaskless, vertical parting line greensand molds. The molding cycle time was 8-11 seconds. The iron was poured into the molds at 2,520°F (1,382°C) and the molds were allowed to cool for about one hour, before shakeout [47].

The shakeout process which the trial cores underwent was 50% shorter than the typical length used at HMAC’s Lawrenceville facility. This truncation was

Figure 3.3 A “part 249” core. The darker color of the sand indicates that this is a “Type 1” core, using lake sand [43].

Figure 3.4 Several “part 249” cores. These are “Type 2” cores, using Wedron silica sand, as their light color shows.
necessary to quarantine the test castings. Unaffected by
the shortened shakeout process, all cores readily and
fully shook out, confirming the hybrid binder’s
excellent shakeout characteristics.

All the castings produced in this test were
subjected to a primary shot-blast step (which is often
followed by a secondary shot-blasting). HMAC
personnel who routinely evaluated “part 249” castings
inspected a batch of parts, in a blind quality test,
containing castings produced using cores with
conventional phenolic urethane and PSU’s hybrid core
sand binder. These inspectors identified 47 good
castings (21% Type 1 and 24% Type 2 cores), from the
batch produced using the hybrid binder system.

The castings produced using the collagen and
sodium silicate binder had an acceptable surface finish,
did not vein (even without antiveining additive), and most importantly they did not exhibit any
erosion from molten iron [47]. (This lack of veining is common to cores using sodium silicate
binder [26].) However, the overall scrap rate was high at 77% (according to Fox, typical scrap
rate for core-related issues is 0.5-5%) [47].

There were several factors which contributed to the high casting scrap rate, when the
hybrid binder cores were used. First, the cores were produced using a “part 249” core box which
was a retired shell core box, and had seen extensive use (see Figure 3.6). It was slightly warped, and moved vertically when opened, which frequently compromised \((i.e.,\text{ cracked})\) the “part 249” cores within. Further, although it had been improved, the box’s venting was not well suited for use with a heavy, water-based core sand binder \((e.g.,\text{ about } 50\% \text{ of the “binder” mass added to the sand is water; therefore, for the amounts of hydrolyzed collagen and sodium silicate hydrate used, a mass of water equal to } 1.3\% \text{ the mass of the dry sand is added})\). Consequently, the “stem” portion of the “part 249” core frequently lacked sufficient core density. These problems resulted in both a high core production scrap rate and also contributed to the high casting scrap rate.

Another factor contributing to the high casting scrap rate was core handling. The PSU cores were handled significantly more than those produced within a foundry. During their lifetime, they were transported over 360 miles (580 km) – from OH to PA, and then within PA (from PSU, to HMAC’s Lawrenceville facility in Tioga, PA). Also, by the time PSU’s “part 249” cores were used at HMAC, they were between 25 and 33 days old, and Fox found their surface hardness had decreased by 30% [47]. Nonetheless, in this casting trial they performed acceptably well, demonstrating the robustness of the hybrid core binder system.
Chapter 4 Core Humidity Resistance

4.1 Introduction

Foundries typically mass produce cores using automated equipment. Although cores are frequently used within a few days, a common requirement is that cores retain strength over a “shelf” \textit{(i.e.} storage\textit{)} time measured in weeks. For example, some sand cores produced via the hot box technique have shelf lives in excess of three months \cite{54}. Furthermore, core storage can be beneficial to some binder systems. For example, commercial PUBC/PUNB cores increase in strength (up to a point) with storage time \cite{28}.

It is well-documented that sand cores bonded with sodium silicate-based binders have poor humidity resistance \cite{26}. Their surface becomes “friable” \textit{(i.e.}, sand grains pop off easily) and their tensile strength drops when stored in humid environments. As a binder, sodium silicate is brittle and highly alkaline and remains water soluble \cite{42}. When investigating core binder condensate hydrophobicity, Zook, \textit{et al.}, found that while phenolic urethane and collagen were hydrophobic, sodium silicate was hydrophilic \cite{55}. While organic additives may help alkali silicate binders resist humidity, their effect may be insufficient \cite{1}. This degradation stands in stark contrast to the established core binder requirement of the absorbance of the minimum amount of moisture during storage or when inserted into the greensand mold (which contains free water) \cite{26}. As Dietert wrote, “[S]urface softening [of a core during storage] due to moisture absorption often erases all other advantages of a core binder” \cite{26}.

During the “part 249” casting trial at HMAC, the PSU team encountered increased core surface friability, caused by moisture absorbance during storage. Fox believed that core softening could be rectified by altering the binder composition \cite{47}. At the time, however, it was
unknown which hybrid binder portion (i.e., collagen or sodium silicate) was predominantly hygroscopic. Although literature indicated that humidity softened sodium silicate bonded cores, in 2005 it was reported that ambient moisture decreased the core tensile strength of GMBOND® collagen binder during storage. Therefore, a series of experiments were proposed to compare the hygroscopicity of collagen to sodium silicate-based binder.

4.2 Materials

4.2.1 Core Sand Binders

As in Sections 2.2.1 – 2.2.2, commercial sodium silicate hydrate (i.e., Cast Clean®) and hydrolyzed collagen (2:1 – water: dry collagen) were used together and independently. As a stand-alone binder, sodium silicate addition was 3.0% (wet); for cores using collagen alone the addition was 3.0% (wet). The hybrid binder was 1.75% (wet) mass sodium silicate and 2.0% (wet) mass hydrolyzed collagen. The two-part ISOCURE™ phenolic urethane binder system was also used added at a 1.03% (wet) mass.

Experiments were conducted in which potassium-lithium silicate was added to sodium silicate. The potassium-lithium silicate solution used was Lithisil® 829, a commercial product of PQ Corporation (Malvern, PA). Compared to the sodium silicate solution which was 42.5% solids by mass, this potassium-lithium silicate solution was 29.3% solids, by mass [56]. In these experiments, Lithisil® 829 was added to sodium silicate at a 1:2 mass ratio.

4.2.2 Mold

An open-faced, dog-bone, standard mold was used to make standard AFS shaped cores for tensile testing. (Another name for this industry-standard test core shape is “dog biscuit” [25].)
As shown in Figure 4.1, the mold array was three rows of three dog-bone, open-faced cavities. The sand-binder mixture was manually compacted into the cavities, and the excess was removed by scraping a flat, wooden stick across the mold’s open surface. The cores were cured by placing the mold assembly into an oven at 110°C (230°F) for one hour. When removed from the oven, the mold cooled for 30 minutes. The assembly was then carefully disassembled, and the dog-bone core samples were removed.

4.2.3 Oven

(See section 2.2.5) All samples were cured in a VWR® Scientific Model 1305U Utility Oven maintained at 110°C (230°F).

4.2.4 Desiccator

Dog-bone cores were placed into a desiccator after curing. A VWR® temperature/humidity meter (model 61161-378) measured temperature and relative humidity within the desiccator. According to VWR International, LLC (Radnor, PA), the meter’s humidity accuracy was ±2–4%, with a range of 25–95%, and a resolution of 1% relative humidity (RH).

Figure 4.1 (a) A top view of a dog-bone core; (b) the dog-bone mold assembly [27].
The cores were placed on a ceramic, perforated plate, within the desiccators. To simulate low-humidity conditions (RH < 25%), the desiccator bottom was filled with desiccant, and a vacuum seal was applied. To achieve high humidity conditions, the desiccator bottom was filled with tap water, to within about 1” (2.54 cm) below the ceramic plate on which the samples sat (see Figure 4.2). Given sufficient time and a sealed lid, the air within the desiccator became saturated with water, yielding a RH ≥ 90%. Although heating the water would have increased the amount of moisture in the gas phase, it was found that even at room temperature the concentration of water in the air sufficiently affected the core strength of all the hygroscopic binders tested [57].

4.2.5 Surface Scratch Hardness Testing

Measuring the scratch hardness of a core’s surface provides an indication of the core’s ability to withstand stocking and handling without losing its integrity or shape [26]. Surface scratch hardness of dog-bone cores was measured using a Dietert Scratch Hardness Tester, in accordance with AFS test procedure 318-87-S (see Figure 4.3). Each dog-bone surface was tested three times, and the average reported. The core’s smoothest side (i.e., the

<table>
<thead>
<tr>
<th>Table 4.1 The range of typical surface scratch hardness readings for various core types [26].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type Mold or Core</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>Dried molds, soft</td>
</tr>
<tr>
<td>Dried molds, hard</td>
</tr>
<tr>
<td>Baked cores, soft</td>
</tr>
<tr>
<td>Baked cores, medium</td>
</tr>
<tr>
<td>Baked cores, hard</td>
</tr>
<tr>
<td>Baked cores, very hard</td>
</tr>
</tbody>
</table>
side pressed against the mold’s flat surface, versus the exposed open face) was always used for surface scratch hardness tests. Table 4.1 provides examples of typical surface scratch hardness values for various sand core types.

### 4.2.6 Sand

The core sand used in these experiments came from Wedron Silica Company (Wedron, IL), and had a specified AFS grain fineness number ranging from 67-73.

### 4.3 Method

Sand and binder were mixed using a commercial-grade Kitchen Aid Mixer, with a flat-beater head. When collagen was used as a partial or sole binder, the sand was preheated to 100°C (212°F) prior to mixing in the hydrolyzed denature collagen. The sand-binder mixture was hand-packed into the dog-bone mold, and the cores were thermally cured. Once the dog-bones were fully cured, removed from the mold, and cooled to room temperature, the surface hardness of at least cores were tested immediately. This represented the surface hardness at “day 0.”

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61 Industrially sand heating is sometimes used to enhance binder solvent evaporation as an alternative to purging the core box with hot air. This is less preferred, however, because it can decrease “bench life” or “work time” [1, 21].
The cores were then stored under different humidity conditions for up to seven days. For every 24 hour period of interest, dog-bone cores were removed from the desiccator and their surface hardness was immediately tested. In some cases, the cores crumbled during testing, yielding a surface hardness value of zero. In this state, these samples represented truly unusable cores.

4.4 Results

As expected, high humidity minimally affected core surface hardness for samples made with phenolic urethane binder. As Figure 4.4 shows, the average surface hardness for dog-bone cores made with 1.03% phenolic urethane binder decreased slightly from their initial surface hardness. Furthermore, this minor loss in hardness did not increase with continued exposure to

![Figure 4.4](image)

**Figure 4.4** The relative surface hardness of dog-bone cores made with 1.03% (wet mass) phenolic urethane binder after exposure to low (< 20%) and high (> 90%) relative humidity. Unless otherwise noted, each sample size is three dog-bones, each sampled three times. Error bars represent one standard deviation.
high humidity.

This slight loss of surface hardness in phenolic urethane bonded cores exposed to high relative humidity is well-known. Core curing method is known to influence moisture sensitivity (e.g., hot box cured cores generally resist humidity better than those cured via warm or cold box methods) [1]. It has also been reported that high humidity can decrease the tensile strength of cores using phenolic urethane; this effect, however, is reversible by drying [58]. In general, however, these humidity resistance experiments confirmed that phenolic urethane core sand binder is relatively unaffected by high humidity during storage.

As Figure 4.5 shows, under low humidity conditions the core surface hardness of dog-bones made with the hybrid sodium silicate and collagen binder had an average surface hardness

![Figure 4.5 The relative surface hardness of dog-bone cores bindered with 1.75% sodium silicate (wet mass basis) and 2.0% hydrolyzed collagen (wet mass basis) after exposure to low (< 20%) and high (> 90%) relative humidity. Unless otherwise noted, each sample size is three dog-bones, each sampled three times. Error bars represent one standard deviation.](image-url)
above that of cores made with phenolic urethane. When exposed to high humidity, however, the surface hardness dropped dramatically after just 24 hours, decreasing until reaching total failure between four and five days of exposure.

To determine the binder ingredient predominantly responsible for surface strength decay, dog-bone cores made entirely with collagen and sodium silicate were tested. As shown in Figure 4.6, the surface hardness of dog-bone cores using solely collagen as adhesive did not exhibit the rapid, dramatic decrease in surface hardness, under high humidity exposure. In fact, even after six days in a >90% relative humidity environment, the average surface hardness of these cores was 25. Further, as shown in Figure 4.7, when sodium silicate alone was used as a binder, surface hardness in the presence of high humidity rapidly dropped, and by the second day was already zero.

It should be noted that the surface hardness of the cores made with sodium silicate, even under low relative humidity, varied quite significantly. Although a uniform process was used to compact and test all the cores in this study, there were certainly variations in each batch. Therefore, to increase the statistical significance of the most important surface hardness readings (i.e., initial hardness [prior to exposure to humidity], and hardness after one and three days in a humid environment), more cores were tested at these conditions.
Figure 4.6 The relative surface hardness of dog-bone cores made with 3.0% (wet mass basis) hydrolyzed collagen after exposure to low (< 20%) and high (> 90%) relative humidity. Unless otherwise noted, each sample size is three dog-bones, each sampled three times. Error bars represent one standard deviation.

Figure 4.7 The relative surface hardness of dog-bone cores made using 3.0% (wet mass basis) sodium silicate after exposure to low (< 20%) and high (> 90%) relative humidity. Unless otherwise noted, each sample size is three dog-bones, each sampled three times. Error bars represent one standard deviation.
4.5 Discussion

These experiments revealed that the sodium silicate portion of the hybrid binder system is more humidity-sensitive than is collagen. Both are clearly affected, however, by high relative humidity. Nonetheless, the surface hardness of cores bonded with sodium silicate decreased more rapidly than those made using collagen.

It was hoped that the cross-linking effect of collagen with the alkali silicate binder would increase the overall moisture resistance, as past research has shown [59]. Although under low-humidity conditions, cores bonded with collagen and hybrid binder had harder surfaces than those made with phenolic urethane, combining hydrolyzed collagen and sodium silicate did not inhibit moisture-induced softening.

Allen also found a mild surface scratch hardness increase when adding collagen to sodium silicate, versus just sodium silicate alone [27]. Allen used HMAC lake sand (versus the Wedron silica sand used in this study), changed the binder content to 2.0% (wet mass) sodium silicate and 1.5% (wet mass) hydrolyzed collagen, and tested cores at 20-40% RH and 80-95% RH. His findings regarding humidity-induced core softening, however, are in good agreement with the results of this study.
It has been reported that lithium silicates produce insoluble films, while sodium silicate remains soluble [42, 43]. One possible reason for this is that lithium has a smaller ionic radius, compared to sodium or potassium [23]. Consequently, to improve core binder humidity resistance, Fox recommended adding potassium-lithium silicate to both sodium silicate and the hybrid, two-part binder system. As show in Figure 4.8, however, in short, three-day experiments, adding potassium-lithium silicate to either mixture did not improve core surface hardness, compared to the results in Figures 4.6 and 4.7.

Figure 4.8 The relative surface hardness of dog-bone cores with (top) 1.0% (wet mass) potassium-lithium silicate added to 2.0% (wet mass) sodium silicate, and (bottom) 1.0% (wet mass) potassium-lithium silicate added to the hybrid binder (1.75% sodium silicate + 2.0% hydrolyzed collagen).
Another method of rendering sodium silicate insoluble is through a second metal oxide anion [42]. Iron oxide and other extenders such as aluminum phosphates, or iron or tin chelates are common core sand binder additions [26, 42]. Nine dog-bone cores were made using 1.75% (wet mass) sodium silicate 2.0% (wet mass) hydrolyzed collagen solution, and 1.75% (dry mass) Fe₂O₃ powder. The dry ferric oxide powder was mixed into the sand first, followed by the liquid sodium silicate and then hydrolyzed collagen. This gave the resultant dog-bone cores a red appearance, as shown in Figure 4.10. As shown in Figure 4.9, however, the addition of ferric oxide did not improve core humidity resistance.

The most effective method of maintaining the integrity of hybrid cores was found by

![Figure 4.10 A dog-bone core produced with silica sand, ferric oxide, sodium silicate hydrate, and denatured collagen.](image)

![Figure 4.9 The relative surface hardness of dog-bone cores with 1.75% (dry mass) Fe₂O₃ dry powder added to 1.75% (wet mass) sodium silicate and 2.0% (wet mass) hydrolyzed collagen binders, after exposure to low (< 20%) and high (> 90%) relative humidity. Each sample size is three dog-bones, each sampled three times. Error bars represent one standard deviation.](image)
Allen. In his work, he found that dog-bones produced using PSU’s binder could regain most of their surface hardness by re-drying at 150°F (65.6°C) for 30 minutes. This supports the statement made by Veinot, et al., that “Soluble silicates are hygroscopic and absorb and desorb water as the ambient humidity varies” [46].

While re-drying is a possible method for re-hardening core surfaces and regaining strength, it requires a significant amount of thermal energy and requires additional core handling. These factors make it an unattractive option to the foundry industry.
Chapter 5 Automated Core Production at PSU

5.1 Introduction

Metalcasting foundries mechanically produce cores in automated processes. While the binder types, mixing techniques, and curing methods widely vary, core blowing is the undeniable, principle tenet of automated core production. The mold is called the “core box.” It exists in two halves, which part either horizontally or vertically, attached to hydraulic or pneumatic pistons which are a part of the core blowing machine.

To make a core, compressed air blows the binder-sand mixture from a storage magazine into the core box. It is expected that blowing will uniformly fill the mold cavity to the desired density. The mixture is then cured, using a gaseous or liquid phase catalyst, or thermal energy (or both). Once the cores have sufficiently hardened, the core box is automatically pulled apart, and the cores can be manually or mechanically removed. Traditionally, cores are stored on rolling carts or racks for movement from the core room to the production line, where they may be inserted into a larger greensand mold.

Core making used to be a skilled art. Core production mechanization, however, has led to highly automated production equipment replacing manual labor [1]. Consequently, although skilled laborers will handle and examine the cores, the core production process requires minimal human interaction or oversight. Therefore, a binder must be robust enough to handle variations in process conditions with minimal outside corrections to enhance production performance (e.g., frequently changing cure times or temperatures; altering blow pressures; vent plugging; etc.).

Before the metalcasting foundries will consider adopting a new core sand binder system, the proposed replacement must be rigorously tested. For example, if a foundry produces almost
exclusively furan shell cores and switches to a water-based binder, their entire core room must be retooled and the laborers retrained. Before undertaking such an expensive endeavor, metalcasting facilities want to be certain that the automation and production output of their core manufacturing lines is not compromised or diminished. Likely the best way to demonstrate a new binder system’s capability is through full-scale production (and subsequent casting) demonstrations (or “trials”).

To evaluate the acceptance of the hybrid core binder system in U.S. ferrous metalcasting foundries, the PSU team planned a second, casting trial at HMAC’s, Lawrenceville, PA, facility. Unlike the previous “part 249” demonstration, however, the PSU team manufactured the cores on campus, using a Harrison Machine Company automated, research-scale core blower. The production goal was 2,000, part “234” (see Figure 5.1) cores. With this many cores, a six hour casting trial could be conducted in Lawrenceville.

5.2 Materials

5.2.1 Core Sand Binder

Cores were produced using a composite mixture of Cast Clean® (i.e., sodium silicate) and hydrolyzed, denatured collagen. The specifics regarding these materials can be found in Sections 2.2.1 and 2.2.2, respectively. Collagen was denatured in heated water at a 2:1 ratio. As noted by Allen, denaturing 100 grams (0.22 lb) of dry collagen (enough for 20 kg [44 lb] of sand) required about an hour [27]. Sodium silicate was premixed into the sand, followed by the collagen solution. The binder mixture was 1.1% (wet mass) sodium silicate and 1.5% (wet mass) hydrolyzed collagen solution. It was considered paramount to reduce the overall binder
concentration to the lowest amount possible, to reduce material cost and avoid core-related gas defects in the resultant metal castings [25].

5.2.2 Core Sand

To increase the applicability of the cores produced for this casting trial, PSU made hybrid bindered cores using the lake sand used by HMAC. This sand was somewhat coarser than the Wedron silica sand predominantly used in bench-scale, laboratory tests at PSU. This sub-angular lake sand had an estimated SiO$_2$ content of 94.58%, a moisture content (MC) of 0.08%, and a loss on ignition (LOI) of 0.17%, with a pH of 7.19 [27]. It should be noted, however, that the in earlier “part 249” casting trial at HMAC both sand types performed similarly (see Chapter 3).

Sand was mixed in 40 to 60 pound (18-27 kg) batches. These had been premeasured into metal buckets, and an electric band heater element preheat the sand to approximately 50°C (122°F), prior to core sand mixing and blowing.

5.2.3 Core Machine

The core machine used at PSU was manufactured by Harrison Machine Company, LLC (Erie, PA; see Figure 5.2). This machine was
specifically produced for core-making research. In the center was the sand magazine, with a hopper above it. Two core boxes could be installed on the unit – one on the left side, one on the right. The right side was equipped with a natural gas burner array to heat a shell core box. The left side had an automatic gassing head.

### 5.2.4 Core Box

HMAC provided a “part 234” core box, as shown in Figure 5.3. This mold produced “part 234” cores, as shown in Figure 5.1. The box was fitted with vents in the upper “T” region of the core, and scratch vents beneath the central barrel. The box was also drilled to accept four, 0.5” (1.27 cm) diameter FIREROD® Cartridge Heaters, made by Watlow® (Winona, MN). Each side of the core box had two heater elements. Each side was controlled by a Watlow® 988 Series controller. The heater element power supply was 240 VAC, 60 AMP.

### 5.2.5 Core Sand Mixer

Industrially, core sand and binder are mixed either via a continuous or batch mixing processes [1, 21]. Batch mixing is best for varying binder levels, offers more operator control, and has a higher mixing efficiency, than continuous mixing [21]. To mix the

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**Figure 5.3** The “part 234” core box used by PSU; (A) through-box vent locations; (B) locations for electric-rod heating elements; (C) core cavity; (D) scratch vents [27].

**Figure 5.4** The TinkerOmega MM100 batch mixer [27].
sand and binder, the PSU team procured a high-speed, MM100 batch mixer produced by Tinker Omega Manufacturing, LLC (Springfield, OH; see Figure 5.4). A proprietary paddle-shaped mixing head blended the sand and binder within the bowl. According to the manufacturer, this mixer required a minimum sand batch size of 35 lb (16 kg) of sand, but could not accommodate more than 70 lb (32 kg). The manufacturer cited an approximate mixing time of 42 seconds. The mixer was powered by a 5 HP, 480 VAC motor. There was no variable speed control on the mixer.

5.2.6 Heated, Compressed Air for Core Curing

A Superheat System was provided by FNI for use with the Harrison Core Machine at PSU. According to FNI, the system allows core cure temperatures in the range of 150-1,300°F (66-704°C). The system is comprised of two units: a control box, and an in-line air heating element, as shown in Figures 5.5 and 5.6, respectively. The control box regulates the volume of air flow to the core box during curing, and regulates the temperature of the downstream, in-line 4 kW, 480 VAC air heater element.

5.3 Method

The core production process began with sand and binder preparation. A premeasured sand mass was heated, using an electric band heater, and the collagen was denatured in a hot water bath. Once this was
achieved, the hot sand was dumped into the batch mixer. With the mixer started, in less than 30 seconds, a premeasured amount of sodium silicate was manually metered into the mixing bowl. The sodium silicate and sand mixed for 60 seconds, to ensure complete coating, and then the denatured collagen was manually added, within 30 seconds. Blending continued for another 60 seconds, and then the mixture was dumped from the mixer bowl into a waiting bucket. This gave a total maximum mixing cycle time of 180 seconds.

Once the mixing step was completed, the mixture was manually dumped into the core machine sand hopper. To initiate a cycle, the core box would pneumatically close, and slide to position itself directly beneath the blow head. Beneath the hopper, a flapper-type valve would automatically open, allowing the sand and binder mixture to drop into the sand magazine. The electrically-heated core box would be automatically lifted up against the rubber-gasket coated bottom of the blow head, creating a temporary seal. Once the flapper valve closed, compressed air at 40 psi (276 kPa) was fed into the magazine, where it fluidized the sand mixture, transporting it into the core box where it was compacted by the air. This blowing and compaction time (i.e., “invest time”) typically lasted 2-5 seconds, depending on the binder.

![Diagram of core production process](image)

**Figure 5.7** The automated core production process, using the Harrison core machine at PSU.
mixture used \(i.e.,\) the higher the water content, the longer the required invest time).

Once the sand and binder had been compacted into the box, the core box slid to the right of the blow head tube. The box sat in this position for approximately 10 seconds, allowing thermal energy from the electrically-heated core box to begin to cure the external surfaces of the cores. After the short dwell time, a gassing head dropped down onto the top of the core box and heated, compressed air was forced through the filled core box. The air heater element within the compressed air line was set to 300°F (149°C).

After three minutes of flow, the air was turned off and the gassing head automatically lifted. Once this occurred, the vertical core box pneumatically opened, and the cores could be manually removed. The total time from a core blow, to removal of the finished product is called “cycle time” and averaged 3.5 minutes.

Before and after each cycle, the external temperature of the core box was measured using a hand-held, Omega® infrared thermometer. Measurements were always taken on the same physical spot on the core box, and from the same distance.

5.4 Results

To build on the initial “part 249” casting trial at HMAC, the goal of the research related in this section was to produce 2,000 cores using the hybrid binder system for a second, larger demonstration. To achieve this high volume production goal, maximum core output with minimal scrap would be necessary. The “part 234” core box had five core cavities. Thus the \textit{de facto} research goal became finding a condition where the two-part binder concentration and automated core production machine settings resulted in the production of five strong cores with a smooth hard surface, every cycle.
As previously discussed, generally cores should have: (1) permanent dimensional stability prior to casting; (2) high strength during intermediate handling and storage; (3) resistance to erosion during pours; (4) high hot tensile strength; and (5) quickly diminishing strength after metal casting solidification, for good collapsibility and shakeout [1]. Acceptable cores must also have no regions of low density, no burned or over-cured areas, and low residual water content.

During core production, only two immediate core-examination techniques could be used: (1) breaking the cores apart, or (2) examining them by sight and touch for defects. Although breaking open one core from every batch provided a more thorough examination, doing so destroyed 20% of the cycle output. Therefore, during production, cores which “looked” and “felt” good were deemed to be acceptable for the casting trial.

In pursuance of the production goal, just under 150 core production cycles were run in about 40 hours. On average, cycle times were 16 minutes. This included the time required to (1) mix new batches of sand and binder (sans the collagen hydrolyzation time\(^\text{62}\)); (2) transport sand; (3) produce the cores; (4) manually remove the cores from the mold; and (5) conduct routine maintenance. Of the 16 minutes per cycle, blowing and curing cores represented only 20% of the core production cycle time (the invest time was just a few seconds, and the average total box dwell time was only 3.5 minutes). Most of the time was spent on carefully removing the cores from the box, and performing maintenance.

It was found that a 60 lb (27 kg) batch of dry sand (plus the binder) lasted for 10 core production cycles. Therefore for this work as a whole, an estimated 900 lbs (408 kg) of sand

\(^{62}\) It was not included, since the denaturing of collagen was achieved with little to no operator interaction.
were used. In total, 415 acceptable “part 234” cores were produced. With each cycle affording
the opportunity to produce five cores, however, the overall average scrap rate was high at 38%.\textsuperscript{63}

Maximum recorded box temperature was 253°F (123°C); the recorded minimum was
84°F (29°C); the average was about 170°F (76.7°F). On average, between both core box halves,
a temperature drop of only 3.7°F (15.7°C)\textsuperscript{64} was observed between the beginning and the end of a
run. In general, one side of the core box tended to lose thermal energy (as measured by an
average 8.2°F [13.2°C] drop in temperature\textsuperscript{65}), while the other slightly gained on average just
under one degree Fahrenheit during a core production cycle. For the range of core box
temperatures observed, no repeatable trend was observed regarding the influence of box
temperature on core production or core quality.

Initially, the first batch of cores was placed on a wooden pallet near the core machine.
Relative humidity in the core production room hovered around 60% (as measured by a VWR
temperature and RH meter). It was soon observed, however, that the cores’ surface properties
deteriorated so rapidly that the cores had to be stored in an extremely low humidity environment
immediately after blowing. This humidity controlled storage environment was provided by the
55 gallon storage drums with integral shelves, designed and fabricated for the “part 249” casting
trial.

\textsuperscript{63} On the final date of core production, the scrap rate dropped just below 30%, whereas on one of the first production
days the scrap rate was almost 50%.
\textsuperscript{64} Sample size (n) = 272.
\textsuperscript{65} n = 131.
5.5 Discussion

5.5.1 The Author’s Work

Since only one previous attempt had been made to mass produce full-scale cores using automated equipment and the hybrid binder, high volume core production at Penn State’s campus required fundamentally learning how to make cores using the Harrison core blower. Although the Harrison core machine was a significant improvement over the much older Redford Carver blower used in Cleveland, OH, the fundamentals of core production with the hybrid binder were still unknown. With a high production goal, however, a delicate balance between determining best production practices and high volume output had to be struck.

Typically, core sands using sodium silicate binder require a high blow pressure - between 90-100 psi (621-689 kPa). According to Ashland, Inc., the preferred blow pressures for cores using ISOCURE™ binder are 35-45 psi (241-310 kPa) [21]. During core production with the hybrid binder for the “part 249” casting trial, blow pressures of 75 psi (517 kPa) were required to completely fill and compact the core box, for three seconds. In this work, however, using the Harrison machine and the “part 234” core box, a blow pressure of only 40 psi (276 kPa) and an invest time of about three to four seconds was used. At the time, this reduction in pressure was attributed to better core box venting and simpler core geometry.66

Perhaps the most significant issues with automated core production using the PSU hybrid binder system were the unacceptably high core scrap rate, long cycle times, and machine clogging issues. Although the scrap rate did eventually drop from 50 to 30% (simply by learning how to make acceptable cores), the scrap rate for the final cycles was still unacceptably high.

66 As will be discussed, Allen also used a low blow pressure, but found that core density was significantly lower than that of identical, “part 234” cores made with phenolic urethane binder [27]. This was believed to be a problem.
A 16 minute core production cycle time is unacceptably long. In 2005, CERP identified long production cycle times as being one of the issues with collagen core binder systems – they were 36% longer than those required for the phenolic urethane binder systems [39]. In those tests, cycle time (under ideal machine conditions) with collagen binder was 2.5 minutes. While most of the long core production cycle time in this work can be accounted for (and was devoted to issues specific to the machine and process), the most basic cycle time of 3.5 minutes is still several times longer than typical, industrial core production cycle times (for example, shell core production cycle times are about 1 minute, and those for PUCB are half that [30]).

A significant portion of cycle time was devoted to manual clean-up of partially-hardened, core sand which hindered flow through the machine. The wet sand and binder in the hopper frequently had to be manually pushed down into the sand magazine. While this increased cycle time, it was also caused by the unusual length of the cycle times, which allowed the binder to dehydrate and harden while sitting in the sand hopper. This prevented it from readily flowing, under the influence of gravity, from the hopper to the magazine, when the blow valve was open. Further, sand would plug the blow holes in the plate at the bottom of magazine, through which it was expected to flow into the core box. These blockages of hardened sand had to be manually cleared before the beginning of each cycle, to ensure a full core box fill.

It is important to note that clogging caused by partially-cured sand and binder blockages is not uncommon when blowing phenolic urethane cores [25]. Because CO$_2$ in the ambient air can cure phenolic urethane binder, these core machines also suffer from obstructions.

Another significant time requirement was physically removing the cured cores from the core box. The industry refers to this as “strip” or “demold” [1]. Although the core will continue
to gain in strength after leaving the mold, prior to removing the core, it should have achieved at least 350 kPa (51 psi) tensile strength, to avoid distortion or other damage during stripping [24, 28]. Although this demolding step is typically automated, it was performed manually during this research. While automation would reduce the time required by this step, most of the cores in this study had to be carefully removed from the box or they would break apart. Thus, manually stripping the cores from the core box added to cycle time but decreased the core scrap rate.

As in the previous trials, humidity caused core properties to degrade, and therefore core storage required special attention. As previously mentioned, in a bid to save the cores, they were stored in vacuum-sealed drums with desiccant. However, this did not slow their degradation. Ultimately, the 350 “good” cores which were produced had to be scrapped. Because of this, it was acknowledged that, to achieve best results: (1) cores had to be made rapidly, (2) stored for a very short period of time, and (3) tested almost immediately.

5.5.2 Subsequent, Relevant Work

The following is a brief summary of Allen’s work, as set forth in his 2014 M.S. thesis. It is relevant and useful to include, because it closely represents the author’s intended future research, and the likely results thereof.

In four days, Allen and associates produced 351 “part 234” cores, and on the fifth day they were transported to HMAC. Two binder mixtures were used to make these cores: 2.0% (wet mass) sodium silicate, and 1.5% (wet mass) hydrolyzed collagen; and 3.0% (wet mass) sodium silicate, and 1.5% (wet mass) hydrolyzed collagen. Allen found that the second mixture retained good scratch hardness after five days of storage.
All cores were stored in vacuum-sealed, 55 gallon drums filled with desiccant immediately after production. However, due to low core density and decreased surface scratch hardness, 107 cores (some from both mixtures) were scrapped on the day of the trial at HMAC.

Interestingly, Allen found that after a truncated shakeout process, the castings poured in molds containing the mixture with the higher sodium silicate content had not shaken out fully. While there certainly may have been many other contributing factors, this author would assert that a 3.0% sodium silicate binder content was too high to achieve good shakeout in an iron foundry.

Despite core softening and shakeout issues, Allen’s “part 234” scrap rate was only 2.5% - a remarkable achievement and a dramatic improvement over the early “part 239” core performance. This time, however, the surface finish of the produced castings was noticeably rougher.

Although these tests closely replicated the initial “part 249” trial, they did not fully demonstrate the emission-reducing properties of the hybrid binder, at the industrial scale. In order to both demonstrate production success and conduct an air emissions (“stack”) test, the casting trial needed to be 12 hours long, using only PSU’s hybrid cores. This would require a minimum of 3,600 cores. Producing this number of “good” cores at PSU would require a very long time, as well as a much more rigorous knowledge of how to: (1) best make the “part 234” cores with the novel binder, and (2) how to store and transport them.

In all his core production, Allen used virtually the same automated core production process as described in Section 5.3, above. The most notable variations in equipment and overall

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67 Allen ended up making 4,666 cores, in nine days.
process was: (1) the employment of a ring compressor, which applied a 42” (water) vacuum on the core box vents; and (2) the enlargement of the blow holes beneath the blow head plate.\textsuperscript{68}

Attempting to identify the variables which could most significantly decrease cycle times, Allen used a fixed binder composition of 3.0\% (wet mass) sodium silicate, 1.5\% (wet mass) hydrolyzed collagen.\textsuperscript{69} He found that the best way to reduce cycle time was by increasing the pressure (but not the temperature) of the hot air forced through the core box during curing. Allen did not investigate air pressures above 25 psi (172 kPa), however, due to a venting peculiarity which created an unacceptably loud whistle noise (about 120 dB) at higher pressures.

Allen’s culminating work was the production of 4,666 cores for a stack air emission test at HMAC, conducted by ARCADIS. Binder composition remained 3.0\% (wet mass) sodium silicate and 1.5\% (wet mass) hydrolyzed collagen solution. Investment blows were four seconds long at 40 psi (275.8 kPa). The wet core sand and binder sat in the box for 15 seconds, before 400°F (204°C) hot air was forced through the box at 20 psi (137.9 kPa). A vacuum was simultaneously applied to the core box. The core box temperature was maintained at 280-330°F (138-166°C), and the total cure time was three minutes.\textsuperscript{70} After being stripped from the box and cooling for 30-45 minutes, cores were wrapped for protection during shipping and were vacuum sealed in 55 gallon drums.

At the time of the casting trial at HMAC, the design of the ferrous metal casting (which used the “part 234” sand core) was changed. Its wall thickness was reduced, thus providing less thermal energy for bond decomposition. Nonetheless, shakeout was good, and no castings were

\textsuperscript{68} The latter of these process enhancements was probably the most significant.

\textsuperscript{69} It is noteworthy that Allen also investigated the effect of reducing the sodium silicate binder addition to 2.0\% (wet mass) which decreased cycle time by 35 seconds.

\textsuperscript{70} By comparison, according to Ashland, Inc., for a 20 lb (9 kg) sand core using ISOCURE™ binder, total cure time should be five seconds [21].
scrapped for core-related issues during this demonstration. The HMAC quality assurance personnel did, however, once again comment on the rougher-than-usual casting surface finish, caused by the PSU cores. Allen hypothesized that this issue was caused by low core density.

Core density is an important but often overlooked property, since it can be tedious to measure. Allen found that “part 234” cores made with Lake Sand and phenolic urethane binder were 50 grams (0.11 lb) heavier than identical cores made with the hybrid binder at PSU. Since the geometry of the cores can be assumed to be identical and the same type of sand was used, this implies that there is more void space within the PSU cores. This could have caused the casting surface defects observed during the HMAC trials, as the excessive expansion and contraction of the hybrid cores increased the surface roughness of the resultant casting.

Although the hybrid binder did not overcome its issue with surface roughness in produced castings, this final demonstration at HMAC did support its merits as a cleaner binder system. At separate times during the casting trial, phenolic urethane cores and PSU’s hybrid cores were run on HMAC’s metal pouring line while air emission data was collected. ARCADIS reported total hydrocarbon (THC), methane, and ethane (VOCs) emission concentrations (in ppm) coming from three baghouses downstream of the casting, cooling, and shakeout line. According to Allen, ARCADIS’s final determination was that switching from the traditional, phenolic urethane core sand binder system to PSU’s novel hybrid reduced THC and VOC concentration by 38.5% and 31.9%, respectively.
5.6 Summary

Successfully producing cores through an automated process is complicated and complex. Much time must be devoted to process development and binder level adjustments prior to mass core production. The importance and merit of this step cannot be overemphasized. Ultimately, the author’s work served as a stepping-stone for future research in this endeavor.

As indicated by Allen’s success, sand cores could be mass produced using the hybrid core binder system. The core machine, core box, and binder addition levels, however, must be carefully tailored to the process.
Chapter 6 Summary

6.1 Key Research Findings Summary

The results of all the work related herein on the hybrid, two-part binder system developed at PSU can be summarized in the following points:

(1) Adding hydrolyzed, denatured collagen to a commercial sodium silicate core sand binder reduces core UCS, after thermal treatment at elevated temperatures (250-1,110°C; 482-2,030°F). As bench-scale core shakeout indicators, these tests confirmed findings from a “part 249” and “part 234” casting trials – *i.e.*, cores made with PSU’s alkali silicate and collagen core binder system had excellent to satisfactory shakeout properties, when compared to phenolic urethane cores.

(2) PSU’s hybrid binder system is capable of (a) mass core production, and (b) has demonstrated full-scale casting production success. The difficulties overcome during the “part 249” casting trial demonstrated that the low-emission hybrid binder was sufficiently robust. Despite worn tooling, hundreds of complex “part 249” sand cores were made using relatively low concentrations of sodium silicate and collagen core binder. Furthermore, although metal casting scrap rate was high during the casting trial, industrial partners considered the binder worth the cost of additional development.

(3) As demonstrated in this work and supported by reviewed literature, ambient humidity has a dramatic and negative effect on the properties of hybrid cores because the hybrid binder system uses sodium silicate. Although cores bonded solely with collagen degrade in the presence of humidity, the portion of the hybrid binder most responsible for core softening is the sodium silicate.
(4) It was confirmed that the hybrid core binder system could be suitable for mass core production, provided sufficient time for process and binder level tuning. The PSU system, however, continued to suffer from core property degradation due to ambient humidity, requiring an elaborate and careful core storage process. Further, although the metal casting scrap rate when using hybrid bonded cores during full-scale trials dropped to an acceptable level, casting surface roughness verged on being unacceptable. This was attributed to low hybrid core density.

6.2 Closing Remarks

The low-emission, hybrid core sand binder developed at Penn State shows significant promise as a replacement to petrochemical core sand binders. Research has proven it capable of significantly reducing foundry VOC and HAP emissions \([27, 47]\). There are three key problems with the hybrid binder system, however, which are preventing it from being adopted by U.S. metalcasting foundries: (1) core decomposition due to humidity; (2) difficulties in automated production; and (3) core density \([27]\). Because this binder system truly presents foundries with the ability to reduce their air pollution, future research should focus on solving these three critical problems as quickly as possible.
Chapter 7 References


[27] J. F. Allen, *Sodium Silicate and Hydrolyzed Collagen as a Hybrid Core Binder for Pollution Prevention in Foundries*, University Park, PA: Penn State University, 2014.


