CHEMICAL ADDITIVE SELECTION IN MATRIX ACIDIZING

A Thesis

by

JASON LEE WEIDNER

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2011

Major Subject: Petroleum Engineering

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ABSTRACT

Chemical Additive Selection in Matrix Acidizing. (May 2011)

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This work proposes to survey new chemical knowledge, developed since 1984, on fluid additives used in matrix stimulation treatments of carbonate and sandstone petroleum reservoirs and describes one method of organizing this new knowledge in a software program using the Visual Basic for Applications programming language. While matrix stimulation treatments have been used in the petroleum industry for over 100 years, the last major review of the technical literature addressing this process occurred in 1984. Currently though, the petroleum industry better understands formation damage; uses different and more chemical additives in matrix stimulation treatments; and understands how some additives interact with one another affecting well performance. As a result, a new and thorough review of the literature regarding chemical additive choices for matrix stimulation treatments will help practicing engineers achieve better results worldwide. Moreover, organizing this chemical knowledge in a software program using VBA allows an engineer to access the information through the Microsoft's widely available spreadsheet program, Microsoft Excel.

DEDICATION

If it takes a village to raise a child, it takes a city to nurture and support a graduate student. My city-like network has several notables. First and foremost I would like to dedicate this work to my wife, Holly Griffin-Weidner, a woman and engineer who toiled day in and day out in the vast natural gas fields of east Texas and northern Louisiana to support my goal of obtaining a graduate degree. Others in my support network include my mother, Kathy Jones; my father-in-law and mother-in-law, Paul and Donna Griffin; my two brothers, Dustin and Trey Weidner; my in-law siblings Ashleigh and Larkin; my extended in-law family, Mimi and Pappy, Scooter and Debbie, Nancy and Larry as well as the Griffin cousins; my mentors, Drs. Hill and Zhu, Dr. Nasr-El-Din and Dr. Sun; my fellow graduate students, who have showed me genuine kindness and friendship throughout my transition from the oil fields to graduate school, and beyond; and lastly, my dog, a nine pound Boston Terrier named Sophie.

For their love and support I am grateful.

NOMENCLATURE

$CaMg(CO_3)_2$	Dolomite, a Carbonate
$CaCO_3$	Calcium Carbonate, also Known as Calcite, a Carbonate
CO_2	Carbon Dioxide
EDTA	Ethylenediaminetetraacetic Acid
FeS	Iron Sulfide
FR	Friction Reducer
H_2SiF_6	Fluosilicic Acid
HBF_4	Fluoroboric Acid
HCl	Hydrochloric Acid
HF	Hydrofluoric Acid
Hg	Mercury
HgS	Mercury Sulfide
Mgal	1000 Gallons
Mn	Manganese
NORM	Naturally Occurring Radioactive Material
SiO_2	Quartz; Silica
$Si(OH)_4$	Silica Gel
SRB	Sulfate Reducing Bacteria
T_r	Reservoir Temperature
VBA	Visual Basic for Applications

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CHAPTER I

INTRODUCTION TO ACIDIZING AND A RECENT HISTORY OF MATRIX

STIMULATION

Considerable research on matrix acidizing exists because of its 100 year history in the petroleum industry. Out of concern for the practicing engineer's often limited specialized chemical knowledge related to matrix acidizing, McLeod wrote a review of the technical literature (1984). Since then, though, the oil and gas industry has gained much knowledge about which mechanisms cause formation damage and has developed more fluid additives. And in response to the number of technological breakthroughs several investigators have attempted reviews of some of the relevant technology (Frick and Economides 1996; Ghalambor and Economides 2002; O'Driscoll et al. 2005; Rae and Lullo 2002, 2003; Xiong and Holditch 1995). One paper, for example, addresses both deep and shallow formation damage. Unfortunately, though, the work focuses the majority of the paper on deep damage, emphasizing hydraulic fracturing technology instead of matrix treatments(Ghalambor and Economides 2002). Another article, in an attempt to describe a formation damage diagnostic software package, addresses the complexity of formation damage diagnosis. But it also fails to identify the chemical rules that guide the software's logic, omitting the information most useful to an engineer attempting to design a matrix treatment (Xiong and Holditch 1995). Two other articles,

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This thesis follows the format of the *Society of Petroleum Engineers Journal*.

which were meant to describe and explain a matrix acidizing additive advisor software package, cited focused critical parts of their review on the products of only one service company (Rae and Lullo 2002, 2003). And one paper focuses on the geology found in one part of the world (Kalfayan and Metcalf 2000; O'Driscoll et al. 2005) while another focuses only on horizontal orientations (Frick and Economides 1996).

As a result, there is an industry need for an update to McLeod's 1984 work based on scientific literature which specifically addresses formation damage mechanisms and acid additives associated with matrix acidizing worldwide. Such a review could potentially help many practicing petroleum engineers design matrix treatments.

Matrix Acidizing Basics: General

As McLeod articulated in his work, matrix stimulation is the use of acid to remove or bypass shallow damage in the well formation with a pumping pressure below fracture pressure (1984). But it is also important to realize that matrix stimulation treatments have other unique characteristics as well:

- They often only attempt to bypass formation damage, rather than remove it.
- They can only reduce the skin factors associated with chemical damage. That is, they will not improve mechanical skin factors such as those associated with the completion or well orientation.
- It is often better to avoid formation damage in the first place rather than attempt to bypass it later with a matrix treatment.

That being said, successful matrix treatments can sometimes be an affordable method to reestablish target production rates given a bottom hole flowing pressure (Stanley et al. 2000).

Matrix Acidizing Basics: Carbonates

Carbonate wells are common and are often comprised of either calcium carbonate ($CaCO_3$) — either as calcite or chalk — or dolomite ($CaMg(CO_3)_2$). And these rocks are historically treated with HCl or, in high temperature applications, a weak acid such as acetic or formic acid. **Figure 1** shows the reactions of each of the carbonate minerals mentioned above with HCl while **Figure 2** shows their reactions with acetic acid. A typical working concentration of HCl in such treatments is 15 wt%. Weak acid working concentrations vary because of their different disassociation constants. **Table 1** shows a list of working concentrations for some mineral acids in carbonate formations (Alkhaldi et al. 2009; Buijse et al. 2004).

$$CaCO_3 + 2HCl \rightarrow CO_2 + H_2O + CaCl_2$$

$$CaMg(CO_3)_2 + 4HCl \rightarrow 2CO_2 + 2H_2O + CaCl_2 + HgCl_2$$
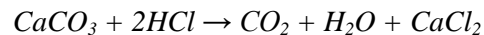
Fig. 1—The balanced chemical equations show how hydrochloric acid (HCl) reacts with calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Note that both reactions result in the production of carbon dioxide (CO_2), which is a gas at some temperatures and pressures.

TABLE 1 – TYPICAL WORKING CONENTRATIONS FOR SEVERAL WEAK ACIDS IN CARBONATE FORMATIONS (Al-Khaldi et al. 2005; Buijse et al. 2004)

Acid	Typical Working Concentration
Acetic Acid	13 wt%
Formic Acid	9 wt%
Citric Acid	< 7.5 wt%

$$CaCO_3 + 2CH_3COOH \leftrightarrow CO_2 + H_2O + Ca^{2+}(CH_3COO^-)_2$$

$$CaMg(CO_3)_2 + 4CH_3COOH \leftrightarrow Ca^{2+} + 4CH_3COO^- + Mg^{2+} + 2CO_2 + 2H_2O$$
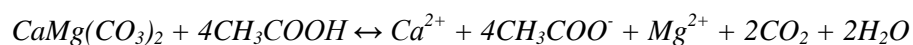
Fig. 2—The balanced chemical equations show how acetic acid (CH_3COOH) reacts with calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Note that both reactions result in the production of carbon dioxide (CO_2), which is a gas at some temperatures and pressures. Also note an equilibrium exists between the forward and reverse reactions, a critical detail of weak acid chemistry.

One concern when using any acid in oilfield operations is the corrosion of well tubulars. Thus operators often choose to pump corrosion inhibitor, a chemical additive electrostatically attracted to the negative charge of the well casing or production tubing, to decrease the rate at which the acid accesses well tubular surfaces (Crowe and Minor 1985). A typical working concentration of corrosion inhibitor is 1-2 wt% of injected acid (Smith et al. 1978). When using corrosion inhibitor it is important to realize that it is not usually dissolved in water-based acid solutions — it is suspended — and floats (Yang et al. 2007). This means most corrosion inhibitor solutions require occasional stirring (every six hours), but not too much or oxygen (O_2) will be added to solution, oxidizing

the relatively benign iron(II) turning it into the relatively malignant iron(III) (Blount et al. 1993). There are several corrosion inhibitors available for use in oilfield operations, each of which protects well tubulars using the same mechanism: by impeding the acid's ability to diffuse to the tubing surface. Because of the unique attraction of corrosion inhibitor to the metal surface, and the corrosion inhibitor's ability to block diffusion of the acid, each putative corrosion inhibitor should be tested with the specific well tubular-acid suite. A coupon test is a common preliminary test to asses a corrosion inhibitor's protective ability. It should be conducted at well pressure and temperature (Joia et al. 2001). Moreover, one can use manganese ion concentration in flowback fluids to monitor the corrosion of well tubulars (Nasr-El-Din, H.A. et al. 2002). Since the only source of manganese in the well system is well tubulars, a spike in manganese ion concentration in produced fluids indicates tubular corrosion.

Even though many wells are completed with low carbon steel, it can sometimes be preferable to complete with nickel- or chrome-based alloys. In that regard, HCl over 15 wt% should not be used with Cr-alloys as HCl is highly reactive with chrome unless specialized steps are taken. The reaction between HCl and chrome is more dramatic as the temperature increases such that for 350°F wells the HCl concentration should be much less than 15 wt% (Nasr-El-DinDriweesh et al. 2003). These rules apply even to wells completed mostly with low-carbon steel and a single chrome pup joint.

Matrix Acidizing Basics: Sandstones

Chemically, sandstones are much more complicated than carbonates because they contain up to 20 different minerals. The common features of sandstones include a portion of calcite ($CaCO_3$), a portion of clay minerals such as montmorillonite, illite or kaolinite, and a portion of quartz (SiO_2). Historically operators use 'mud acid,' a mixture of HCl and hydrofluoric acid (HF), to stimulate sandstone formations. A common working concentration of mud acid is 12 wt% HCl and 3 wt% HF, though the ratio of HCl to HF can range from 4:1 to 9:1, with the HF concentration rarely exceeding 5 wt% (O'Driscoll et al. 2005; Thomas et al. 2002). Investigators have shown the effects of HF concentration on the permeability of Berea Sandstone cores (Economides et al. 1993; Smith and Hendrickson 1965). Others have shown the effects of HF concentrations on offshore treatments (Brannon et al. 1987; Economides et al. 1993). It is common to use 50 to 200 gal/ft of target formation for the HCl/HF stage of a mud acid matrix treatment (Economides et al. 1993; O'Driscoll et al. 2005).

When designing such treatments it is critical to precede the mud acid stage with a stage of HCl (no HF) in sufficient quantity to completely dissolve all carbonates present in the target volume of the formation. If mud acid is allowed to react with carbonate minerals then a formation damaging calcium fluoride (CaF) precipitate will form (Brannon et al. 1987). Some investigators suggest not treating sandstones whose carbonate mineralogy exceeds 15% with a matrix acid job because of this issue. Moreover, it is also critical to know if the carbonates present are the cementing material in the sandstone. If they are, dissolving them with HCl will destabilize the sandstone

grains resulting in potentially expensive and operationally troublesome sand production. Thus, mud acid matrix stimulation should be reserved for sandstone formations that have less than 15% carbonate minerals, where the carbonates are not the cementing material, and that have shallow chemical damage which can be bypassed by a matrix job.

Once the HCl pre-flush removes all carbonate minerals, the main stage HCl/HF mixture creates a complex series of reactions, which has been summarized by several authors (Economides et al. 1993; Gdanski 1998; Gdanski 1999; Gdanski and Shuchart 1996; Li et al. 1998; Shaughnessy and Kunze 1981; Shuchart 1995; Shuchart and Buster 1995; Williams and Whiteley 1971), the most important being the creation of fluosilicic acid (H_2SiF_6) and its reaction with the so called 'fast-reacting minerals.' It is the most important reaction because it explains how HF penetrates so deeply in the formation and how silica gel ($Si(OH)_4$), a precipitate, damages the formation during a mud acid job. Moreover, H_2SiF_6 is a weak polyprotic acid that partially disassociates, forming equilibrium between the acid and the salt forms of the compound.

Some investigators have developed buffered solutions that generate HF *in situ*. One such system uses fluoroboric acid (HBF_4), another uses aluminum chloride ($AlCl_3$) and the third uses phosphonic acid. One benefit of the HBF_4-based system is the control of formation fines. Studies show that HBF_4 solutions can coat formation grains, stabilizing fines in place (Crowe 1986). Other studies show, though, the HBF_4 system does not penetrate deeper into the formation than traditional mud acid over 150ºF. One advantage of the phosphonic acid-based system is that the salt form of the acid stabilizes precipitates from dropping out of spent acid, causing some damaging chemical species to

be produced in flowback fluids (Di Lullo and Rae 1996; Kume et al. 1999). A thorough review of each of these three HF systems exists (Al-Dahlan et al. 2001).

Another concern when stimulating sandstones through a matrix treatment is the swelling of formation clays. Clays have a layered structure with many exposed oxygen atoms, giving each layer an electrostatically negative charge (Hibbeler et al. 2003). The clay volume increases when its original crystalline structure is invaded by water molecules or non-clay cations, both of which are attracted to the oxygen atoms (Civan 2007; Hibbeler et al. 2003). The general strategy for swelling control is through the dramatic decrease of non-clay water molecule or ion invasion. This is typically achieved by using either a cationic surfactant, which binds to the clay surface decreasing foreign ion diffusion rates into the clays, or by using chloride salts in the treatment fluid. When the chloride concentration of the treatment fluid is comparable to that of the clay, the diffusion rate of fluid ions decreases and the clay does not swell. This is an important detail in the matrix stimulation of sandstone reservoirs using HCl/HF mixtures because some researchers have shown sodium and potassium fluosilicate precipitate out of spent acid, causing formation damage (Thomas et al. 2001). Thus, operators who plan to stimulate their sandstone formations with HCl/HF treatments and who also want to use salt to control clay swelling would be wise to use ammonium chloride (NH_4Cl) instead of commonly used sodium (NaCl) or potassium chloride (KCl). This will allow for clay swelling control while decreasing the risk of fluosilicate damage because ammonium fluosilicate (NH_4SiF_6) is more water soluble than the sodium (Na_2SiF_6) or potassium variety (K_2SiF_6) (Gdanski 1994). One thing to consider, though, is ammonium chloride

is slightly acidic. Some service companies also offer a chemical marketed as KCl-substitute, which is $NH_3R^+Cl^-$, where the R-group is a small alkyl. It is functionally equivalent to ammonium chloride for clay swelling purposes. A common working concentration for ammonium salts for clay control is 5 wt% (Al-Araimi and Jin 2006; O'Driscoll et al. 2005; Thomas et al. 2001).

This chapter highlighted the importance of several factors when designing a matrix acidizing treatment. **Tables 2** and **3**, below, summarize the results.

TABLE 2 – SUMMARY LIST OF FORMATION DAMAGE CONCERNS FROM CHAPTER ONE
1. Corrosion inhibitor is critical when using any acid, otherwise dramatic well tubular degradation will occur.
2. High HCl concentrations can dramatically corrode Cr- and Ni-based alloys.
3. Insufficient HCl pre-flush will result in CaF damage in sandstone acid treatments.
4. Acid treatments should not be applied to sandstones with calcite concentrations over 15%.
5. Some sandstone clays can swell during a matrix treatment.
6. Sodium and potassium fluosilicate can precipitate out of spent acid in sandstone treatments if a sodium- or potassium-based salt is used to control clay swelling.

TABLE 3 – SUMMARY LIST OF FLUID RECOMMENDATIONS FROM CHAPTER ONE
1. Carbonates are treated with HCl.
2. Sandstones are treated with HCl/HF mixtures in the main stage.
3. Sandstones are treated with an HCl pre-flush to avoid the formation of CaF, except in the case where iron is present in the sandstone mineralogy. Chelating agents should be used instead.
4. Ammonium chloride or other similar NaCl or KCl substitutes should be used to control clay swelling in sandstones to minimize fluosilicate-based precipitation reactions.
5. All acids require the use of corrosion inhibitor to avoid dramatic tubular corrosion.
6. High concentrations of HCl should not be used with Cr- or Ni-based alloys.
7. Corrosion inhibitor solutions should be stirred every six hours. No more and no less.

CHAPTER II

IRON-RELATED FORMATION DAMAGE, THE IMPORTANCE OF TUBING

PICKLING AND CONSIDERATIONS FOR HIGH TEMPERATURE WELLS

Iron from well tubulars and mineralogical iron are two potential sources of formation damage in acidizing jobs. Investigators studied how these iron ions differ and concluded that those from well tubulars is usually of the ferric type, having a +3 charge, while those from the formation is of the ferrous type, having a +2 charge (Coulter and Gougler 1984; Taylor et al. 1999a; Walker et al. 1991). Moreover, iron from the formation is only sometimes encountered while iron from the tubulars unavoidably results in at least 5,000 ppm ferric iron solution being injected into the formation during acid jobs, even with proper corrosion inhibition (Coulter and Gougler 1984; Taylor et al. 1999a; Walker et al. 1991). This is a significant finding for several reasons. First, it implies that core flood experiments whose goal is to mimic an acidizing job might be run with a minimum of 5,000 ppm ferric iron in order to represent the fluid entering the formation. Second, ferric and ferrous irons precipitate at different pH values. As can be seen by **Figure 3**, ferrous iron begins to precipitate out of solution at around pH 1 while ferrous iron precipitates at over pH 7. And considering the buffering effect of CO_2 present in spent acid, which buffers to approximately pH 5, only ferric iron should be considered the damaging iron source (Crowe 1985). This implies a possible method for addressing the damaging effects of ferric iron; reduce it to the ferrous form. Thus, some researchers suggest doing just that (Taylor et al. 1999b).
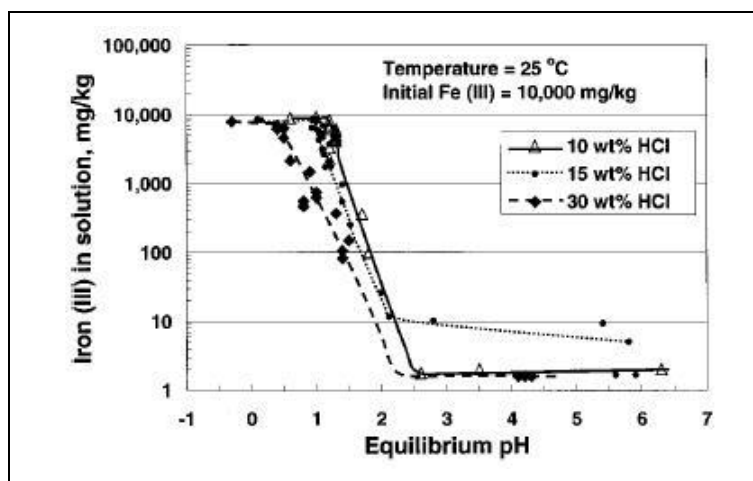
Fig. 3—A graph of iron (III) in solution plotted against pH. The original iron (III) concentration was 10,000 mg iron (III)/kg solution. Since spent acid in carbonate reservoirs are buffered by bicarbonate ions, the pH is about 5 (Crowe 1985), meaning iron (III) precipitates. Iron (II) does not precipitate out of solution until a pH of around 8 (Crowe 1985). The chart is a figure from Taylor et al (1999b).

If an operator is treating a well with a sulfur source — either from formation H_2S or from H_2S produced from sulfate reducing bacteria (SRBs) — then they have additional concerns for formation damage because of the risk of precipitation of iron sulfide (FeS) and elemental sulfur (S_8) (Nasr-El-Din, H.A. et al. 2002). **Figure 4** shows the reactions of ferric and ferrous iron with H_2S to form FeS and, in the case of ferric iron, S_8. To minimize these damaging precipitates an operator has a few options.

$$Fe^{3+} + S^{2-} \rightarrow FeS(s)$$
$$16Fe^{3+} + 8H_2S \rightarrow S_8(s) + 16Fe^{2+} + 16H^+$$

$$Fe^{2+} + H_2S \rightarrow FeS(s)$$

Fig. 4—The reactions of ferric and ferrous iron ions with H_2S to form FeS and, possibly, S_8.
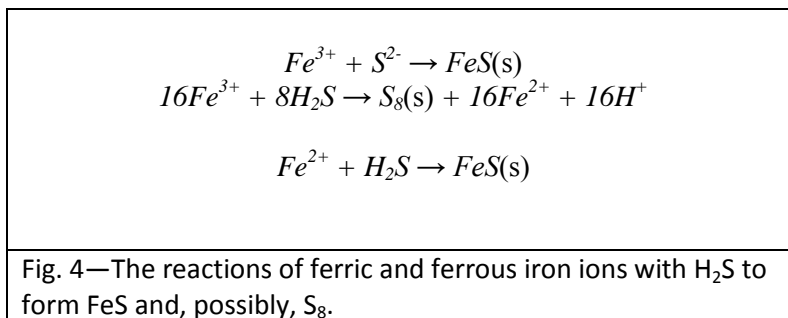
First, they can operationally minimize iron contamination by using a properly selected corrosion inhibitor and by minimizing the tubing's contact with live acid. Following a well designed coupon procedure should assist in regard to selecting a proper corrosion inhibitor. Even with good corrosion inhibition, though, a longer exposure time between live acid and well tubulars will result in high ferric iron concentrations in the fluid. This is particularly true in high temperature applications. Second, an operator could use a reducing agent to convert the ferric iron, Fe(III), to ferrous iron, Fe(II), in an attempt to minimize the amount of elemental sulfur produced. Elemental sulfur precipitation is expensive to remove from the formation.

Third, an operator could use a chelating agent to bind as much iron as possible, making it unavailable for reaction with H_2S. Chelating agents bind Fe^{3+} because of their unique chemical structure. See **figure 5** for the structures of three common chelating agents.

Fig. 5—The structure of three common chelating agents, each in their neutral form: citric acid, EDTA and diethylene triamine pentaacetic acid (DTPA). Citric acid is only a chelating agent below 200°F and can precipitate out of solution when Ca^{2+} ions are present.
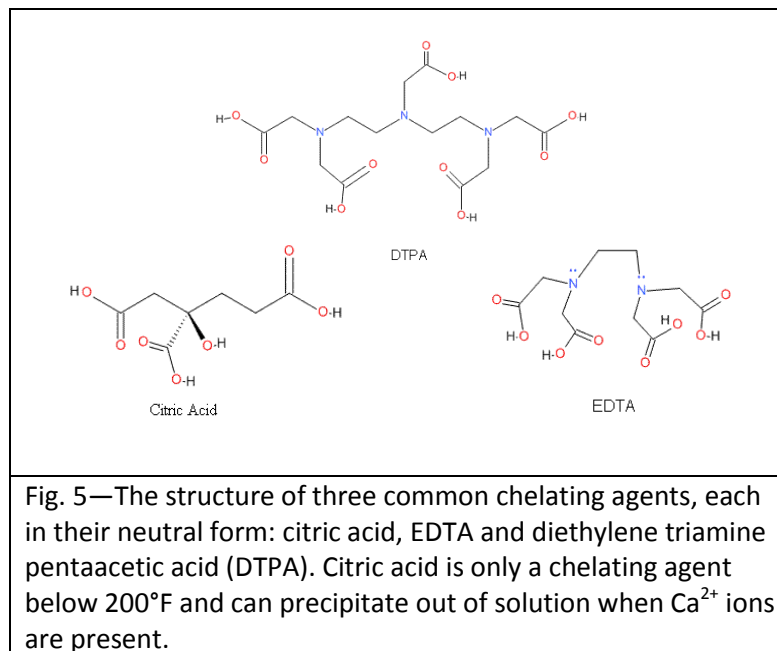
To make a chelating agent work as an iron control agent (ICA) the working solution must be at the proper pH and must be able to survive, structurally, in both live and spent acid solutions. As the pH of a chelating agent decreases, the molecule becomes more anionic, increasing its ability to bind Fe^{3+}. See **Figure 6** for a progression of ethylenediaminetetraacetic acid's (EDTA's) electrostatic charge as its pH changes. EDTA has the additional benefit of acting like a reducing agent at pH > 12 (Brezinski 1999).

Fig. 6—This figure shows how ethylenediaminetetraacetic acid's (EDTA's) charge changes as the pH of its solvent changes. In the top row, from left to right, the charge starts at minus four in solutions of pH higher than 10.4. It changes to a minus three charge until pH 6.1, minus two at about pH 2.7, (second row) minus one at about pH 2 and is a neutral molecule at pH 1.5. Note, too, the structure can have a positive one or two charge if the two nitrogen atoms are protonated at even lower pH values.

Fourth, an operator can use an H_2S scavenger minimizing the hydrogen sulfide available for reaction. There is a review of H_2S scavengers available (Nasr-El-Din, H.A. et al. 2002).

Some wells also form a sulfide precipitate not with iron but with mercury (HgS). This relatively unusual sulfide precipitate is treated differently than FeS but forms because of similar chemical reasons and has been known to appear in some gas wells in the Middle East (Bingham 1990).

A typical working concentration for EDTA is 10 wt% (Huang et al. 2003; Mahmoud et al. 2010), while 1 wt% is typical for reducing agents (Taylor and Nasr-El-Din 1999) and 0.2 – 2 wt% for H_2S scavengers (Nasr-El-Din, H.A. et al. 2002). It is

critical to ensure the suite of fluids chosen to address an iron and H_2S problem are all compatible with one another as well as with the well system itself, including well tubulars and the reservoir. Particular care should be used when using citric acid as calcium citrate can precipitate out of solution (Alkhaldi et al. 2009).

The Importance of Tubing Pickling

One other source of iron from well tubulars is not a corrosion product but is, instead, mill scale, otherwise known as rust. Chemically, mill scale is Fe_3O_4, making it a source of ferric iron ions, the iron ions that precipitate in spent acid and cause formation damage. An extensive study of mill scale in well tubulars showed that for young tubing of moderate length nearly two tons of iron can be injected into the formation using only 100 gallons of 15 wt% HCl. Even more iron is deposited in the formation if the acid is more concentrated, if the formation is hotter, or if the tubing is older, longer or bigger. The results of the study show a simple pickling job can prevent much of this formation damage by simply rinsing the tubing with acid before starting the injection treatment (Al-Mutairi 2004). This works well because HCl is an excellent solvent of mill scale. Also, because of the variability of mill scale size within the tubing it is important to monitor the pickling treatment to ensure the complete removal of Fe_3O_4. One can determine if the pickling treatment has ended by seeing a spike in manganese ion concentration (Mn^{2+}), signifying the onset of tubular corrosion (Nasr-El-Din, H.A. et al. 2002).

Moreover, there are often other chemicals present in the tubing before an injection treatment, pipe dope being especially common. Studies suggest pipe dope is often overused (McLeod Jr. et al. 1983). Considering its greasy and viscous composition it can cause significant formation damage if injected into the reservoir. As a result pickling jobs should include a stage of organic solvent to remove any residual pipe dope in the well tubulars before the acid is used to dissolve mill scale. Some researchers even suggest strictly monitoring pipe dope use, slowing consumption by supplying only a one inch brush for application. A study of the chemical composition of various pipe dopes and their solubilities exists (Nasr-El-Din, H.A. et al. 2002). A typical loading of organic solvent in tubing pickling treatments is 100 gal terpene or xylene for 1,000 ft tubing (O'Driscoll et al. 2005).

For Wells in High Temperature Carbonate Formations

High temperatures can cause a decrease in the effectiveness of corrosion inhibition. In response, the petroleum industry now uses corrosion inhibitors that can withstand higher temperatures, or uses corrosion inhibitor intensifiers, surfactants that increase the strength of corrosion inhibitor-metal bond (Do Carmo Marques and Mainier 1994).

In high temperature applications operators should also be careful to adjust the corrosion inhibitor and corrosion inhibitor intensifier loadings throughout the job based on formation cooling caused by the injection of relatively cool acid into a relatively hot formation. If wellbore cooling is not taken into account too much corrosion inhibitor or

corrosion inhibitor intensifier will be used and the excess will be pumped into the reservoir. Not only will decreasing the loading save money in chemical costs, it will also avoid formation damage caused by corrosion inhibitor and corrosion inhibitor intensifier, chemicals that cause water wet formations to become oil wet (Crowe and Minor 1985). Entire texts address wellbore temperature changes due to injected or produced fluids have been published (Hasan; and Kabir 2002). Some have also directly measured wellbore temperature as a function of time during fluid injection treatments (Nasr-El-DinDriweesh et al. 2003). In cases where too much corrosion inhibitor or corrosion inhibitor intensifier has been pumped into the well, mutual solvent can be used to reestablish water-wet conditions. Working concentrations of mutual solvent should be less than 10 wt%, 5 wt% being typical (Crowe and Minor 1985). There is no additional chemical benefit to running mutual solvent at concentrations over 10 wt%.

Additionally, carbonate formations do not require HCl for matrix stimulation as wormholes can be created using organic acids (Buijse et al. 2004) or chelating agents (Fredd and Fogler 1998). In fact, these alternative fluids are preferable in some high temperature applications for several reasons. First, the high corrosion rate between well tubulars and HCl cannot always be satisfactorily mitigated using corrosion inhibition additives, even with corrosion inhibitor intensifiers. Second, in high temperature applications the reaction rate between calcite and HCl is so fast that a weaker acid creates better wormhole growth per dollar of injected fluid. And lastly, some operators choose to use non-low carbon steel alloys, such as those with chrome or nickel, which

are particularly sensitive to corrosion with acids. In these cases stimulation with

chelating agents might prove to be the better option.

See **Tables 4** and **5** for a summary of the formation damage concerns and fluid

recommendations from this chapter.

TABLE 4 – SUMMARY LIST OF FORMATION DAMAGE CONCERNS FROM CHAPTER TWO

1. Iron ions from well tubular corrosion are a source of formation damage, even with proper corrosion inhibition.
2. Any sulfur source, when combined with iron ions from well tubulars, will result in some FeS precipitation.
3. Some gas wells have mercury present in the formation, risking HgS precipitates if a sulfur source is present.
4. Mill scale, also known as rust, is a major source of formation damaging iron ions.
5. Chemicals other than mill scale, present in well tubulars before the treatment, can also be a source of formation damage. Pipe dope is of particular concern.
6. The overuse of corrosion inhibitor and corrosion inhibitor intensifier can cause the formation to become oil-wet.

TABLE 5 – SUMMARY LIST OF FLUID RECOMMENDATIONS FROM CHAPTER TWO

1. A reducing agent can help prevent iron ion precipitation in acid treatments.
2. Chelating agents can help keep some potentially formation damaging iron irons in solution.
3. EDTA, a chelating agent, also acts as a reducing agent at some pH values.
4. An H_2S scavenger can help decrease the amount of hydrogen sulfide available for the creation of FeS, a damaging precipitate.
5. A pickling treatment should occur before each acidizing job.
6. Tubing pickling procedures should begin with an organic solvent for pipe dope.
7. Tubing pickling usually uses HCl in its main treatment. No matter the acid used, the removal of mill scale, also known as rust, is key.
8. Manganese concentration can be used to identify tubular corrosion and, thus, the end of the pickling job.
9. HCl is not required to stimulate carbonate formations. Chelating agents can be used and might be ideal in high temperature wells.
10. Corrosion inhibitor and corrosion inhibitor intensifier loadings should be decreased with time for high temperature wells. This avoids the wettability changes associated with pumping too much corrosion inhibitor or corrosion inhibitor intensifier in a well that cools down throughout the treatment.

CHAPTER III

FORMATION DAMAGE FROM SCALES

A change in pressure, temperature, pH or fluid ionic strength, or a mixture of two incompatible waters can cause scale precipitates to form. The first set of well system changes is often associated with carbonate scales while the second suggests sulfate or sulfide scaling.

Carbonate Scales

Common forms of carbonate scales include calcium carbonate ($CaCO_3$) and iron carbonate ($FeCO_3$). Iron carbonate will be present if there is 5-10% CO_2 in the reservoir fluids or in CO_2 injection fields, and the iron is often a result of tubular corrosion (Gougler Jr. et al. 1985). A less common carbonate scale is strontium carbonate ($SrCO_3$) which has the additional risk of being radioactive because of the presence of radium as radium carbonate ($RaCO_3$) (Mously et al. 2009).

Carbonate scales form in areas where CO_2 bubbles out of solution, precipitating scale according to the series of reactions found in **Figure 7** (Nasr-El-Din et al. 2004; Yuan et al. 2001). Since the scale forms when CO_2 comes out of solution it is often found in locations with a notable pressure drop such as near a gravel pack, an electronic submersible pump inlet or at the depth where hydrostatic pressure becomes low enough to allow CO_2 to bubble. The CO_2 present in wellbore fluids can come from multiple sources including reservoir fluids; a byproduct of the reaction of acid and formation

carbonate minerals; or from CO_2 injection. Fortunately, carbonate scales are readily dissolved by HCl, organic acids and chelating agents (Nasr-El-Din et al. 2004).

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow HCO_3\text{-} \leftrightarrow CO_3^{-2}$$
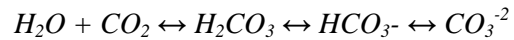
Fig. 7—The equilibrium between dissolved CO_2 and carbonate ions requires that if the concentration of dissolved CO_2 decreases, CO_3^{-2} concentration decreases as well. The CO_2 concentration often decreases in regions of the well system with significant pressure drop (and the gas bubbles out), forcing the carbonate ions to precipitate in the form of a scale.

Sulfate and Sulfide Scales

Sulfate scales often form when sea water mixes with formation waters. Sea water is often a good source for sulfate ions (SO_4^{2-}) while formation waters often contain the divalent cations of calcium, barium and strontium, leading to the formation of relatively insoluble sulfate salts ($CaSO_4$, $BaSO_4$, and $SrSO_4$) (Civan 2007; Clemmit et al. 1985).

While there are equations available for the accurate prediction of sulfate scales, the chemical removal of sulfate scales is often quite expensive because it requires chelating agents. HCl does not remove sulfate scales, nor does HF. As a result much care is taken to prevent the formation of such scales, removing them mechanically when they do form.

Sulfide scales form through a different mechanism than sulfate scales. In sour fields water and hydrogen sulfide (H_2S) react to create sulfuric acid (H_2SO_4). The sulfuric acid then reacts with iron (Fe), lead (Pb), zinc (Zn) or mercury (Hg) to create formation damaging sulfide salts (FeS, PbS, ZnS, and HgS) (Civan 2007; Kelland 2010). The lead and zinc ions can be introduced to the well system through the overuse of pipe dope, while iron is often from well tubulars and mercury from the formation (Nasr-El-Din, H.A. et al. 2002). One or several of these scales can be present in a well system.

Scale Prevention and Mitigation

While it is often cheaper to remove scales from the wellbore or a pipeline through mechanical means such as milling, jetting, or even through the application of ultrasonic energy waves, there are chemical approaches to scale removal. One such approach is through the use of chelating agents (Fink 2003). Another method is through the chemical prevention of scale formation through the use of scale inhibitors. While the specific mechanism of how scale inhibitors work is not completely understood, it is known that it interferes with crystal formation and/or nucleation depending on the specific inhibitor (Clemmit et al. 1985; Nasr-El-DinSaiari et al. 2003; Smith et al. 2008; Yuan et al. 2001). Many scale inhibitors are available, the unifying feature being they are hydrophilic (Fink 2003; Kelland 2010).

See **Tables 6** and **7** for a summary of the formation damage concerns and fluid recommendations from this chapter.

TABLE 6 – SUMMARY LIST OF FORMATION DAMAGE CONCERNS FROM CHAPTER THREE
1. Carbonate scales are expected in wells with 5-10% CO_2 in solution, no matter the source of the carbon dioxide.
2. Iron from well tubulars can combine with carbonate ions to form iron carbonate scales.
3. Strontium carbonate is less common but can be radioactive because of the occasional presence of radium ions.
4. Carbonate scales often form in locations with considerable pressure drops.
5. Sulfate scale can form when formation waters mix with sea water.

TABLE 7 – SUMMARY LIST OF FLUID RECOMMENDATIONS FROM CHAPTER THREE
1. Carbonate scales are readily dissolved by HCl, organic acids and chelating agents.
2. Neither HCl or HF dissolve sulfate scales.
3. Scale inhibitors, often a phosphonate, can be used to prevent sulfate scale formation.
4. Chelating agents can remove many sulfide scales.

CHAPTER IV

PROBLEMS ASSOCIATED WITH BACTERIA

Bacteria have long been a problem in hydrocarbon production and exploration causing a variety of operational issues. First, bacteria are large compared to many pore throats, so their existence in the target formation decreases permeability (Hayatdavoudi and Ghalambor 1996). Secondly, some bacteria are associated with the corrosion of downhole tubulars and hardware because of their production of H_2S, a poisonous and corrosive gas (Kane and Surinach 1997). H_2S also decreases the value of produced hydrocarbons and its biogenic production can sour whole fields (Khatib and Salanitro 1997).

Since the 1980's, much has been learned regarding the interactions between bacteria, hydrocarbons and hydrocarbon-bearing zones. First, petroleum microbiologists discovered that microbes are indigenous to only a subset of the world's hydrocarbon reservoirs because many are too hot (Kashefi and Lovley 2003; Stetter et al. 1993) or too salty (Grassia et al. 1996) to sustain life. Petroleum microbiologists also confirmed microbial infestation in reservoirs that were too hot but whose near wellbore region was cooled because the injection of relatively cool fluids into a relatively hot formation (Hasan and Kabir 2002; Ollivier and Magot 2005).

Microbiologists also discovered that microbes introduced to formations through injection operations are from water sources likely to contain microbes that evolved to survive in biologically hot temperatures, such as those who live near deep sea hot water

vents (Khatib and Salanitro 1997; Stetter et al. 1993). In other words, the infestation of a reservoir by non-indigenous microbes likely occurs because of the injection of untreated or unfiltered sea water.

Moreover, petroleum microbiologists conducted research on the diversity of both indigenous and non-indigenous petroleum microbial life. Their findings show that some bacterial populations produce H_2S while others do not. And for those which do, they prefer to consume nitrate (NO_3) to sulfate (SO_3) (Voordouw 2003). This has led some operators to supplement their stimulation fluids with nitrate (Telang et al. 1997; Voordouw 2003). Some have even suggested alternating injection wells with biocide and nitrate in order to manage an indigenous microbial population instead of eliminating it (Ollivier and Magot 2005) and treating or filtering the injection water .

Moreover, researchers have elucidated the mechanism through which microbes corrode steel tubulars: a reduction-oxidation reaction between biogenic H_2S and iron from well tubulars (Khatib and Salanitro 1997).

See **Tables 8** and **9** for a summary of the formation damage concerns and fluid recommendations from this chapter.

TABLE 8 – SUMMARY LIST OF FORMATION DAMAGE CONCERNS FROM CHAPTER FOUR
1. Bacteria often cause pore throat plugging, dramatically decreasing formation permeability.
2. Some bacteria produce H_2S, a poisonous and corrosive chemical that can be a source of sulfur for precipitation reactions.
3. Bacteria can cause dramatic wellbore tubular corrosion.

TABLE 9 – SUMMARY LIST OF FLUID RECOMMENDATIONS FROM CHAPTER FOUR

1. Biocides can be used to control bacteria populations.
2. Bacteria are often introduced into injection wells from contaminated sea water. Filtration can remove the bacteria.
3. Nitrate supplements can be used to control H_2S formation by bacteria, as it is a preferable food source to sulfate.

CHAPTER V

POTENTIAL PROBLEMS WITH VISCOUS DIVERTERS, POLYMER SOLUTIONS

AND EMULSIFIERS

Stimulation operations often call for the use of viscous fluids or foams. Viscous fluids are normally used for fluid diversion while foam treatments have additional uses in the treatment of large productive intervals. Even though these fluid options provide additional features to a putative stimulation treatment they also have their own unique drawbacks.

Viscous Fluids and Polymer Solutions

Viscous diverters come in a variety of options including man-made polymer solutions, natural polymers and viscoelastic surfactants – but they all operate the same way: either by viscosifying the fluid themselves or by connecting the long chain-like molecules to increase fluid viscosity (Fink 2003; Klelland 2010; Moradi-Araghi 2000). Man-made polymers often are polyacrylamide or one of its derivatives, used in conjunction with a cross-linker to link the polyacrylamide chains together (Ahmed et al. 2008; MaGee et al. 1997; Smith 1995). Natural polymers are very similar to polyacrylamide in that they are also large molecules used with cross-linkers, but the long chains are made of naturally occurring products like xanthan, starch, guar, or one of guar's many derivatives (Ash et al. 1983). Viscoelastic surfactant is unique, chemically, in that there is no cross-linker required for viscosification. Instead, viscoelastic

surfactant is a solution of small surfactant molecules that, when in a solution of proper pH and proper Ca^{2+} ion concentration, bind together creating long string-like structures. Eventually the string-like structures will coordinate with Ca^{2+} ions effectively cross-linking the fluid, increasing its viscosity (Ali et al. 2005; Lungwitz et al. 2007; Nasr-El-Din and Samuel 2007).

Research has shown that formation damage occurs as a result of the use of polymer solutions because the polymers leave residue at the formation face and in the pore throats (Lungwitz et al. 2007; Lynn and Nasr-El-Din 2001; Taylor and Nasr-El-Din 2003). Thus, in order to minimize this damage, the practicing engineer would be wise to ensure the polymer is adequately destroyed when it is no longer needed. Man-made polymers can be 'broken' with oxidative breakers (Kelland 2010). There are two common oxidative breakers used in the oilfield: persulfate breakers and peroxide breakers. Both work by creating highly reactive free radicals in solution that react with the polymer backbone, breaking it. These breakers also have a temperature range in which they function well.

An operator can use oxidative breakers to break natural polymers, but they can also use enzymes instead. Enzymes are specific to the polymer they break and have many important issues to consider for use in operations (Luyster et al. 2000). First, they are temperature sensitive. Second, they are often sensitive to heavy metal concentrations which is an important detail considering many cross-linkers are made with heavy metals (Kelland 2010). Third, enzyme treatments require long incubation periods (Al-Yami and Nasr-El-Din 2009; Luyster et al. 2000).

Viscoelastic surfactant can be broken through a reversal of the polymerization reaction. Thus, a change in pH or Ca^{2+} ion concentration will decrease fluid viscosity. Many times this is done by flow back of hydrocarbons or through the injection of mutual solvent solutions (Lungwitz et al. 2007; Nasr-El-Din and Samuel 2007). If viscoeleastic surfactant is not completely removed from the formation, it is possible for the matrix to become oil-wet.

Foams

Stimulating long productive intervals with regular HCl can be expensive and still leave much of the wellbore unstimulated, thus some operators choose to stimulate using a foamed solution. Foams are created by mixing an energized fluid with a surfactant (Kelland 2010). A concern with foam treatments, whether for diversion or the stimulation of large open intervals, is the potential for water blockage.

See **Tables 10** and **11** for a summary of the formation damage concerns and fluid recommendations from this chapter.

TABLE 10 – SUMMARY LIST OF FORMATION DAMAGE CONCERNS FROM CHAPTER FIVE
1. All polymer solutions leave residue at the formation face, decreasing permeability.
2. Viscoelastic surfactant solutions can cause formation wettability changes; changing water-wet formations to become oil-wet.
3. Foams can cause water blockage.

TABLE 11 – SUMMARY LIST OF RECOMMENDATIONS FROM CHAPTER FIVE
1. Oxidative breakers, either peroxide or persulfate breakers, can be used to break many polymers.
2. Enzymes can be used to break some natural polymers, though there are cases when enzymes cannot be used such as high temperature, high salinity, high metal concentration or low pH solutions.

CHAPTER VI

COMMON OPERATIONAL MISTAKES

It is critical to ensure all acid storage tanks are clean before pumping an acidizing treatment. Some recommend first removing all organic contaminants with an organic solvent, then washing the tanks with steam and finally rinsing them with the same type of acid being used for the job. Rubber-lined tanks are the best as they reduce the amount of iron pumped into formation. All acid transport vehicles need to be clean as well. There should not be any solids in the tanks or transport vehicles (McLeod 1989).

The acid itself should also be quality controlled before its use in a matrix treatment. The HCl should not be contaminated with iron before use. Before adding corrosion inhibitor, HCl solutions with low iron concentrations will appear yellow or light green. Corrosion inhibitor has a very dark brown color so once it is added the acid will have a dramatically darker appearance even if not contaminated with iron. It is important to minimize iron in the HCl before pumping it into the wellhead because even with proper corrosion inhibition a minimum of 5,000 ppm ferrous iron will be present in the acid, potentially causing damage.

If the acid is mixed with seawater then all additives should be tested for solubility in highly saline solutions.

Electrostatic Charge and Matrix Stimulation

An operator can avoid many formation damaging mistakes by knowing the electrostatic charge of all components of their well system. Recent studies show that cheap friction reducer, an anionic molecule, is often electrostatically incompatible with cheap biocide, a cationic molecule. At best both additives will be functional in the treatment fluid but only less so. At worst, they precipitate completely rendering both completely ineffective and damaging (Rimassa et al. 2009). Another common mistake is the use of negatively charged friction reducer and positively charged scale inhibitor (Rimassa et al. 2009). Anionic scale inhibitors exist so it would be better to use them with an anion friction reducer (Fink 2003; Klelland 2010).

An operator should always know the electrostatic charges of common well components. Sandstone formations are negatively charged because of the clay. Carbonate formations are positive (Das 2007). Low-carbon steel is always negatively charged, thus necessitating that corrosion inhibitors always have positive charges. Anti-sludging agents are necessarily negatively charged as well, implying that they should be pumped with additional corrosion inhibitor, if used.

Simple Mistakes Causing Formation Damage

Many simple errors can lead to dramatic formation damage. For example, sandstone formations receiving a mud acid treatment are likely to become damaged if an insufficient large HCl pre-flush is pumped. The resulting damage is from CaF precipitation.

In the special case of iron-laden sandstone formations, the use of an HCl pre-flush will damage the well. Chelating agents must instead be used to prevent iron precipitates from forming.

Using KCl or NaCl to control clay swelling in drilling operations on a well that will eventually receive a mud acid treatment will exacerbate fluosilicate precipitation during the HF stage, too. Instead, use ammonium chloride salts for clay control. Also, the damaging precipitates that form from a mud acid treatment can be minimized with the use of a H_3PO_4-buffered HF acid system.

While corrosion inhibitor is needed with any acid treatment, using too much will cause a water-wet formation to become oil-wet. It is easy to pump too much corrosion inhibitor in hot formations because the injected fluids cool the reservoir. As a result, the corrosion inhibitor loading should decrease throughout the job. It is also easy to use too little corrosion inhibitor, causing formation damaging iron participates to form, because the corrosion inhibitor floated out of solution in the stock tanks on the surface. Acid tanks should be stirred every six hours, but not more because it will needlessly introduce O_2 to the solution, risking other damaging reactions.

Formation damage will result if the tubing is not pickled before the stimulation job. Some of the damage will be from iron because of the presence of rust in the well tubulars, while some is likely to be from pipe dope. Moreover, if it is a sour well, FeS and elemental sulfur are likely to damage the formation as well. And elemental sulfur cannot be economically removed once it forms.

Formation damage will also occur if HCl is used in a well with Cr-based tubulars, even if the Cr-based tubulars only comprise a couple of feet of the completion.

Biocide is not always needed in treatment fluids, but if it is, too much can cause damage because the biocide itself can precipitate if present in high concentrations.

Samples from a Putative Well System

Operators should be aware of several notable dangers associated with samples from well systems. First, some scales are radioactive, especially carbonate scales. Second, flow back fluids are not always pH 7. Wells treated with weak acids will always have slightly acidic pHs and weak acids at high temperatures are highly reactive. Moreover, spent acid solutions from carbonate formations will have slightly acidic pHs as well because of the buffering effects of CO_2. Carbon dioxide is present in all spent acid from wells with carbonate rock in the formation.

See **Table 12** for a summary of the formation damage concerns from this chapter.

TABLE 12 – SUMMARY LIST OF FORMATION DAMAGE CONCERNS FROM CHAPTER SIX
1. Inadequately clean acid storage containers can cause formation damage by the introduction of contaminants, organic or otherwise.
2. Iron contamination of fresh HCl can exacerbate iron precipitation-based formation damage.
3. If salt water is used to create acid solutions, all additives should be tested for efficacy in saline solutions with attention towards solubility.
4. Anionic friction reducer and cationic biocide are electrostatically incompatible and result in a precipitation reaction.
5. Anionic friction reducer and cationic scale inhibitor are electrostatically incompatible and results in a precipitation reaction.
6. Anionic anti-sludging agents and cationic corrosion inhibitor are electrostatically incompatible but are both required in some cases. In such situations, additional corrosion inhibitor loadings should be used.
7. Over stirring corrosion inhibitor at the surface can introduce O_2 in solution, which will convert benign iron ions to malignant ones, resulting in unnecessary iron precipitation damage.
8. Under stirring corrosion inhibitor solutions at the surface will result in corrosion inhibitor floating out of solution and being pumped at insufficient concentrations. This will result in unnecessary well tubular corrosion and iron-related formation damage.

CHAPTER VII

THE ACID ADVISOR USING VISUAL BASIC FOR APPLICATIONS (VBA)

To help the practicing engineer organize all of the newly discovered chemical

rules when designing an acid matrix treatment, I created the Virtual Lab Acid Adviser.

The Acid Adviser is a software package written in Visual Basic for Applications (VBA),

the programming language used to build applications in Microsoft Excel (Excel). This

approach for application development allows a user familiar with Excel to use the Acid

Adviser with ease.

VBA is an object-oriented programming language, meaning its syntax refers to

specific components of the Excel application. For example, when trying to change the

value displayed in a cell in a spreadsheet, a programmer must use the line

"Worksheets("Sheet 1").Cells(j, k).value = Z" where *Sheet 1* is the name of the

worksheet which contains the cell of interest, *j* and *k* are the row and column of the cell's

address, and *Z* is the new value of the cell. *Z* can be a character, a string of characters, a

number or one of many other kinds of data stored in Excel's object model. To

understand the names of Excel's components such as *worksheets*, *cells*, *row* and

columns, etc.; their properties such as *value*; and how to refer to them, it is critical to

learn Excel's object model. A new programmer to VBA might use John Walkenbach's

Excel 2007 Power Programming with VBA (Walkenbach 2007b), an easy to read book

that addresses the basics of the Excel object model and many useful programming

techniques. Moreover, this book includes an introduction to programming for non-

programmers hoping to learn VBA. Walkenbach is the author of another book, *Excel 2007 Charts* (Walkenbach 2007a), that should be used when wanting to programmatically develop any Excel chart using VBA. There are many components in an Excel chart that are unique to charting, requiring a specialized vocabulary for the chart-related object model. *Excel 2007 Charts* will help the new programmer learn this specialized vocabulary, thus empowering them to develop VBA code that controls Excel charting.

Two other useful books are *VBA and Macros for Microsoft Office Excel 2007* (Jelen and Syrstad 2007) and *Word 2007 Document Automation with VBA and VSTO* (Driza 2009). The Jelen and Syrstad book is another great introduction into the Excel object model but includes many techniques that are not included in Walkenbach's *Power Programming*. And Driza's text addresses a specialized topic: automating Microsoft Word 2007 using Excel. There are not many texts on the topic, so this book is especially valuable. With it a new VBA programmer can learn how to generate Microsoft Word documents using values and inputs contained in a Microsoft Excel spreadsheet, all through VBA programming. This was the principal text used in the generation of the Treatment Summaries from the Virtual Lab's Acid Adviser.

Software Interface

The Adviser has a graphical interface, which allows a user to quickly see which components of their well system have been considered in the design of the matrix treatment and which types of formation damage need to be prevented. See **Figure 8** for a

screen capture of the basic user interface of the Acid Adviser and **Figures 9-11** for a

closer view of each of the interface's components.
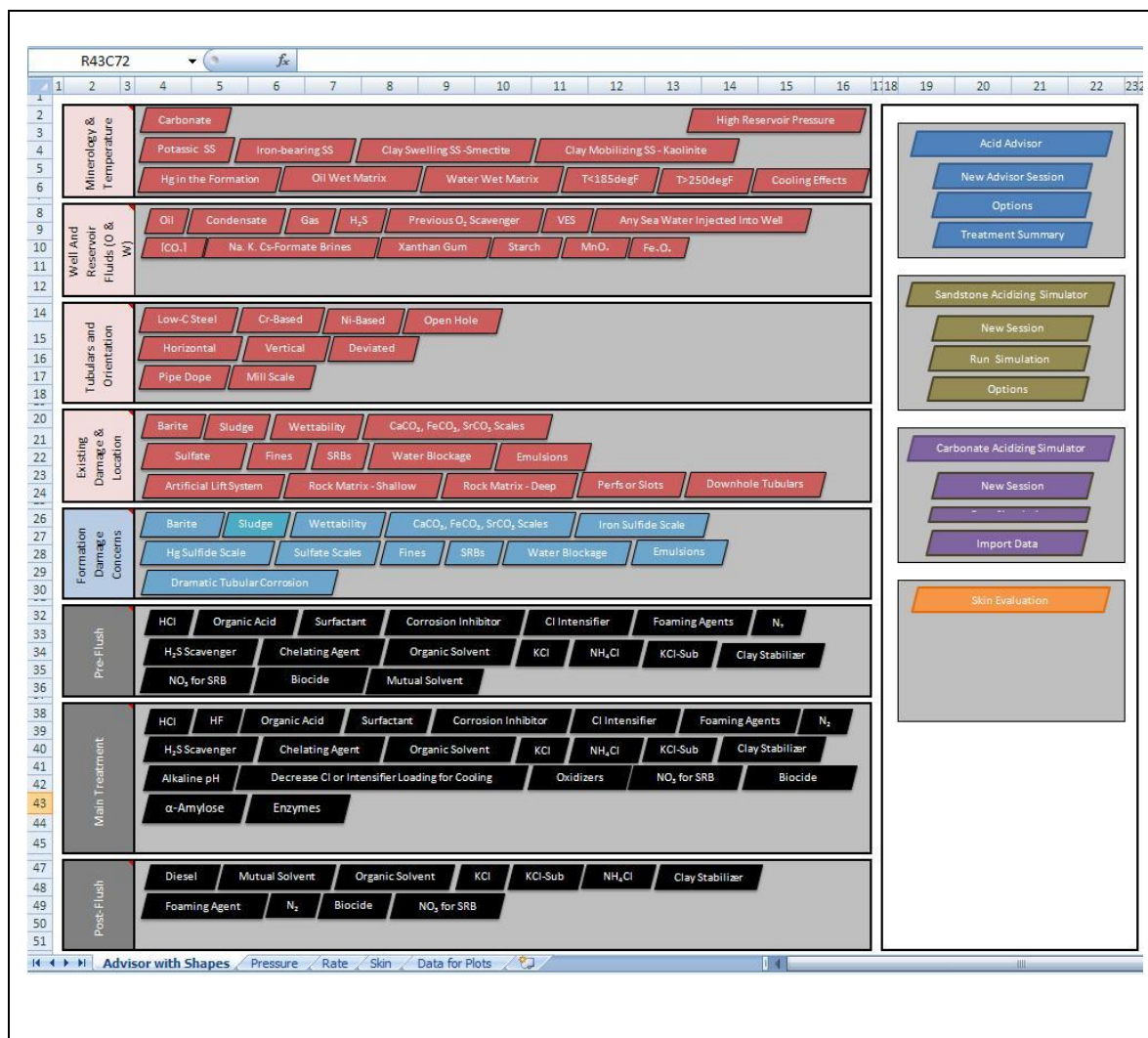
Fig. 8—A screen capture of the Acid Adviser graphical user interface. The well system inputs are represented but red buttons while outputs are represented by light blue and black buttons. Light blue buttons represent potential formation damage concerns while black buttons represent fluid treatment recommendations broken down by pre-flush, main treatment and post-flush stages. The buttons found in columns 18 through 23 on the right hand side of the screen are used to control the software globally because the Acid Adviser is part of a larger Virtual Lab software package. The dark blue buttons at the top of these global controls direct the user through the Acid Adviser.

40
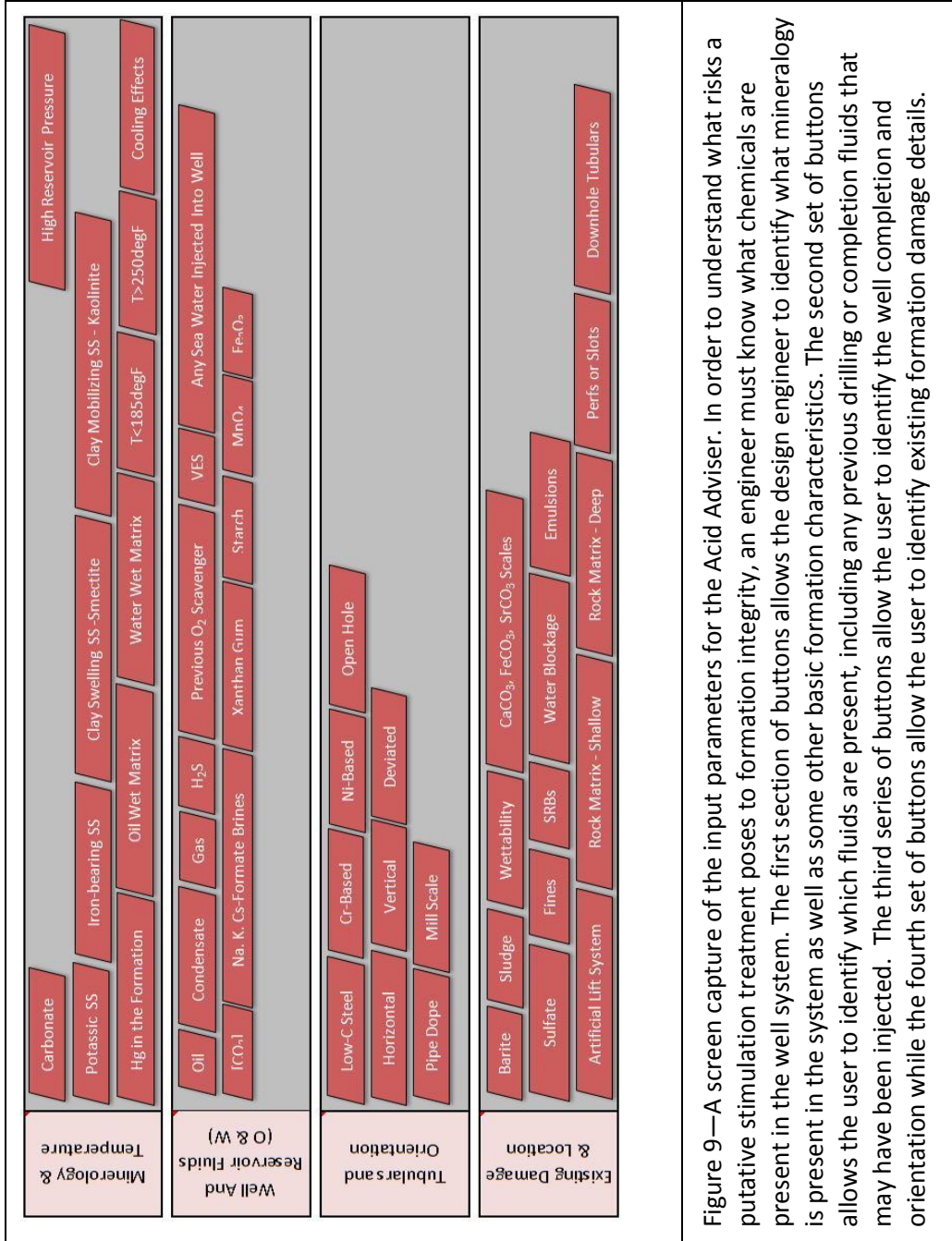
Figure 9—A screen capture of the input parameters for the Acid Adviser. In order to understand what risks a putative stimulation treatment poses to formation integrity, an engineer must know what chemicals are present in the well system. The first section of buttons allows the design engineer to identify what mineralogy is present in the system as well as some other basic formation characteristics. The second set of buttons allows the user to identify which fluids are present, including any previous drilling or completion fluids that may have been injected. The third series of buttons allow the user to identify the well completion and orientation while the fourth set of buttons allow the user to identify existing formation damage details.
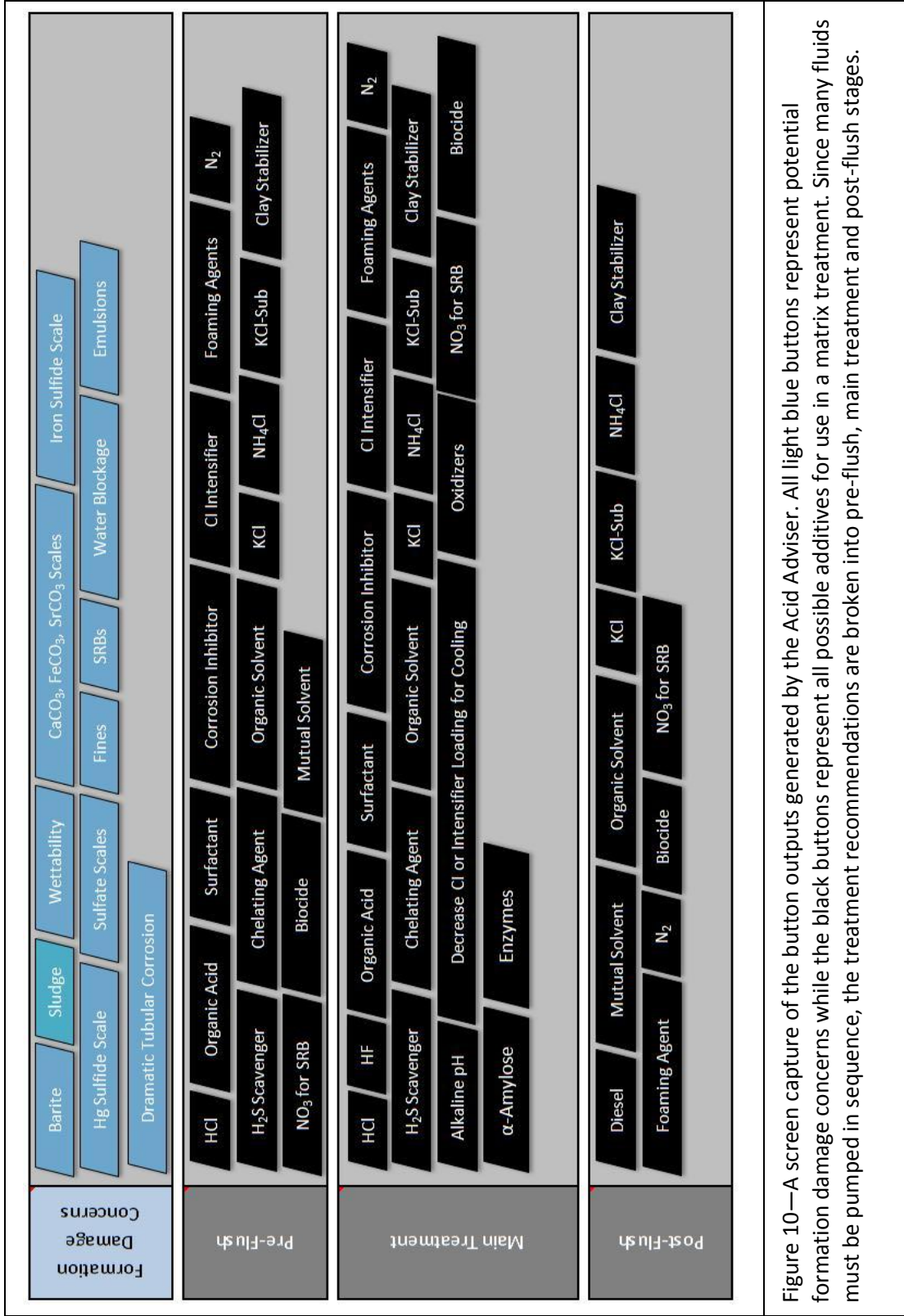
Figure 10—A screen capture of the button outputs generated by the Acid Adviser. All light blue buttons represent potential formation damage concerns while the black buttons represent all possible additives for use in a matrix treatment. Since many fluids must be pumped in sequence, the treatment recommendations are broken into pre-flush, main treatment and post-flush stages.
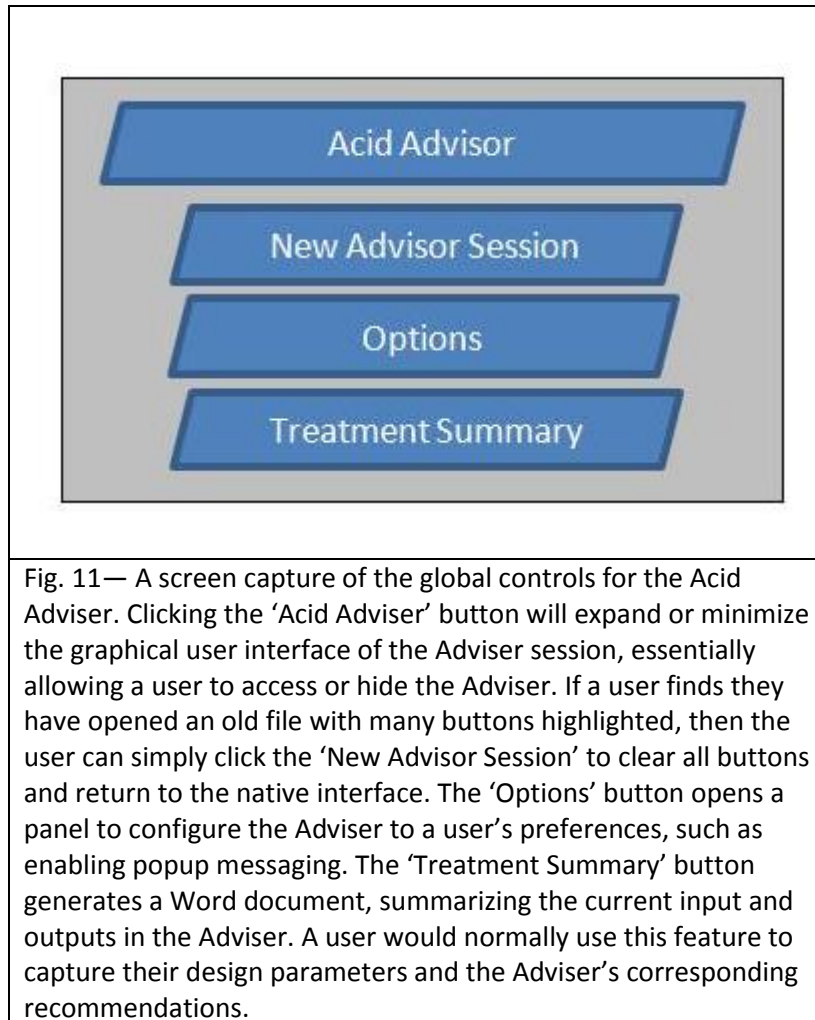
Fig. 11— A screen capture of the global controls for the Acid Adviser. Clicking the 'Acid Adviser' button will expand or minimize the graphical user interface of the Adviser session, essentially allowing a user to access or hide the Adviser. If a user finds they have opened an old file with many buttons highlighted, then the user can simply click the 'New Advisor Session' to clear all buttons and return to the native interface. The 'Options' button opens a panel to configure the Adviser to a user's preferences, such as enabling popup messaging. The 'Treatment Summary' button generates a Word document, summarizing the current input and outputs in the Adviser. A user would normally use this feature to capture their design parameters and the Adviser's corresponding recommendations.

The Acid Adviser can accomplish two basic tasks: (1) recommend fluid additives given well system chemistry and (2) compose a Treatment Summary of the inputs, outputs and common working concentrations of recommended additives. It does each of these by gathering the input data, passing them through a series of functions and sub-routines, and performing a series of tasks.

List of Functions, Sub-Routines and Flow of Control

Every time a user clicks an input button the Acid Adviser executes one function and four sub-routines. See **Figure 12** for the flow of control through the functions and sub-routines. See **Table 13** for a list of the functions and sub-routines, as well as their inputs and outputs.

Fig. 12— The flow of control through the functions and sub-routines accessed by the Acid Adviser when a well system input button, such as 'Carbonate,' is clicked. When the button is clicked the sub-routine Button_Click is executed, where 'Button' is replaced with the name of the input parameter clicked. And the Button_Click sub-routine itself executes one function and three additional sub-routines, in the order shown. The Flag function takes two inputs and provides an output value. By definition sub-routines do not return values; only functions do.

TABLE 13 – SUB-ROUTINES AND FUNCTIONS EXECUTED WHEN AN INPUT BUTTON IS CLICKED		
Function/Sub-Routine Name	Inputs	Outputs
Sub Button_Click()	None	None
Function Flag(x)	x, data type Integer	0, 1, 2, 3, 4 or 5
Sub Color(x, shp)	x, data type Integer shp, data type Shape	None
Sub Future_FormationDamage()	None	None
Sub ChemicalSelection()	None	None

The Button_Click() Sub-Routine

The Acid Adviser requires knowledge of the chemicals present in the entire well system to determine which acid and which additives to include in a matrix treatment. These chemical inputs can be mineralogy, tubular composition, chemicals present in the formation from drilling or completion procedures or any other chemical present in the well system. In order to keep track of each of these chemical inputs, a user identifies them by clicking each component, highlighting its appearance. See **Figure 13** for an example.

Fig. 13— Screen captures of the Carbonate button 'on' (top, in green) and 'off' (bottom, in red). A single click will transition the button from one state to the other.
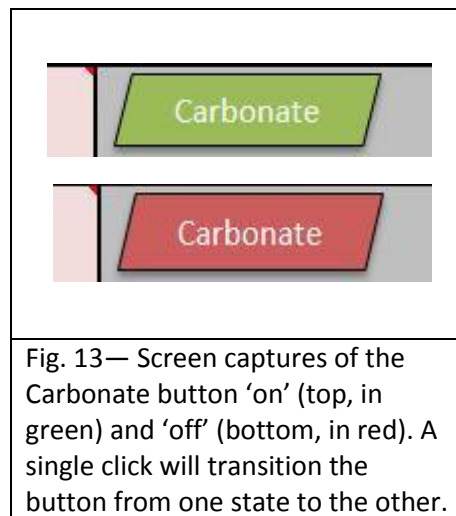
The name 'Button_Click()' is a little misleading because a search of the Acid Advisor VBA code will return no Button_Click() sub-routine. Instead, one might find Carbonate_Click, HighReservoirPressure_Click, or one of 46 similarly named sub-routines based on the input parameters available in the Acid Advisor. What all of these sub-routines have in common are they allow the Adviser to know which components have been identified as being present in the well system. Take Carbonate_Click() as an example, looking at **Figure 14**. First, the sub-routine declares Carbonate as a variable of data type Shape, signPost as a variable of data type Integer, and initializes the variable Carbonate to a shape on the active worksheet. Then Carbonate_Click() sets the value of variable signPost to the return value of the Flag function if passed the Carbonate variable. In other words, Carbonate_Click() passes the Carbonate variable to the flag

function, which returns a value, and then Carbonate_Click() sets the returned value to

the variable signPost. In the next line of the code Carbonate_Click() passes two variables

to the Color sub-routine, variables signPost and Carbonate. Carbonate_Click then

executes the Future_FormationDamage and ChemicalSelection sub-routines.

```
Sub Carbonate_Click()
Dim Carbonate As Shape
Dim signPost As Integer
Set Carbonate = ActiveSheet.Shapes("Carbonate")

signPost = Flag(Carbonate)
Call Color(signPost, Carbonate)
Call Future_FormationDamage
Call ChemicalSelection

End Sub
```

Fig. 14— The VBA source code of the Carbonate_Click() sub-routine,
a portion of the Acid Adviser.

No matter which input button is clicked, each Button_Click sub-routine works

the same way. It declares a shape variable, passing it to a function and a sub-routine, and

then executes two other sub-routines. See **Table 14** for a list of all inputs available in the

Acid Advisor. There is a Button_Click sub-routine for each of them.

TABLE 14 – A LIST OF INPUT PARAMETERS FOR THE ACID ADVISOR			
Mineralogy & Temperature	Well and Reservoir Fluids	Tubulars and Orientation	Existing Formation Damage
Carbonate	Oil	Low-C Steel	Barite
Potassic Sandstone	Condensate	Cr-based	Sludge
Iron-bearing Sandstone	Gas	Ni-based	Wettability
Clay Swelling Sandstone	H_2S	Open Hole	Carbonate Scales
Clay Mobile Sandstone	O_2 Scavenger	Horizontal	Sulfate Scales
High Reservoir Pressure	VES	Vertical	Fines
Hg in Formation	Sea Water	Deviated	SRBs
Oil-Wet Matrix	CO_2	Pipe Dope	Water Blockage
Water-Wet Matrix	Formate Brines	Mill Scale	Emulsions
Temperature<185°F	Xanthan Gum		Artificial Lift System
Temperature>185°F	Starch		Rock Matrix-Shallow
Cooling Effects	MnO_4		Rock Matrix-Deep
	Fe_3O_4		Perfs or Slots
			Downhole Tubulars

The Flag( ) Function

By definition, a function returns a value while a sub-routine does not. In the case of the Flag function, it returns a value of 0 to 5 depending on what kind of shape is passed to it. The goal of the Flag function is to identify whether the selected input parameter is 'on' or 'off.' Whichever state the parameter is in when clicked the Flag function immediately switches it to the opposite state. In other words, if the parameter was 'off' when clicked, the Flag function will recognize the 'off' state and pass a variable whose value indicates that the button should now be 'on'.

Since the Adviser is a visual tool, each of the different parameters of the system is identified by a different color given its section in the interface. In other words, the 'off' state for the Carbonate parameter ─ which is found in the Mineralogy &

Temperature section ─ is a different color than the 'off' state for the Sludge parameter, which is found in the Formation Damage Concerns section. Additionally, a button could be found in neither of these two sections. It could be located in the Fluid Recommendation section instead. Since there are three possible sections for a button, there are three different 'off' colors and three different 'on' colors. That makes a total of six possible values for the Flag function; six values between 0 and 5, inclusive.

The Color( ) Sub-Routine

The Color() sub-routine works hand-in-hand with the Flag() function. While the Flag() function identifies the current button's state and assigns a value to a variable, the Color() sub-routine gives the value an actual color. In other words, the Color() sub-routine is where a programmer who wishes to change the colors presented by the button states would alter the Acid Adviser code.

The Future_FormationDamage( ) Sub-Routine

One of the features of matrix stimulation that make it so complicated is that the stimulation treatment itself can cause considerable formation damage if designed or executed improperly. To address this particular concern the Acid Adviser specifically highlights potential future formation damage. The chemical rules controlling fluid incompatibilities are contained in the Future_FormationDamage() sub-routine. Like all sub-routines, it returns no value. It also requires no input variables. **Table 15** lists all of the chemical rules governing the logic in this sub-routine. If other chemical

incompatibilities are discovered, a future programmer would choose to add those new

chemical rules to this section of the Acid Adviser source code.

TABLE 15 – A LIST OF CHEMICAL RULES GOVERNING FUTURE FORMATION DAMAGE CONCERNS IN THE ACID ADVISER
1. Current barite damage implies future barite damage because of impartial removal.
2. The use of formate brines implies no barite damage is present because formate brines dissolve barite.
3. The presence of oil in the well system implies a concern for future sludge damage.
4. If the formation is water-wet or made of sandstone, then wettability changes are a concern because of the required use of corrosion inhibitor.
5. There is a concern for water blockage if treating a gas well.
6. Fines migration is a concern if the formation contains sandstone with known fines problems.
7. Carbonate scales are a concern if there is carbon dioxide in the well system or if it is a carbonate well.
8. Sulfate scales are expected if sea water is ever injected into the well.
9. Formation damage from iron sulfide (FeS) scales is a concern if there is a source of iron and a source of sulfur.
10. HgS is a concern if it is a gas well with Hg in the formation and there is a sulfur source.
11. Dramatic tubular corrosion is expected if CO_2 encounters low-C steel or if HCl encounters Cr-based tubulars.

The ChemicalSelection() Sub-Routine

The ChemicalSelection() sub-routine is the heart of the Acid Adviser, as this is where the logic guiding the fluid recommendations exists. The code is broken into three sections: pre-flush, main treatment and post-flush. **Tables 16-18** show the chemical rules guiding the fluid recommendations. Table 16 shows the pre-flush rules; 17 shows the main treatment rules; and 18 the post-flush rules. If, in the future, a programmer wants to add or change the rules guiding the Acid Adviser's fluid recommendations, this is the sub-routine that should be altered.

TABLE 16 – A LIST OF CHEMICAL RULES GOVERNING PRE-FLUSH FLUID RECOMMENDATIONS IN THE ACID ADVISER

1. If carbonate or sandstone is in the well system, HCl is recommended in the pre-flush.
2. Organic acid is recommended if it is a high temperature carbonate well.
3. Corrosion inhibitor is recommended if an acid is recommended.
4. Corrosion inhibitor intensifier is recommended if it is a high temperature well.
5. Foaming agent is recommended if it is a horizontal well.
6. H_2S scavenger is recommended if H_2S or SRBs are present in the well system.
7. Chelating agents are recommended if the well is a high temperature carbonate.
8. KCl or KCl-substitute is recommended with clay swelling sandstone formations.
9. Clay stabilizer is recommended with a clay mobile sandstone formation.
10. Biocide and NO_3 are recommended if there is a known SRB problem.
11. Mutual solvent is recommended if it is an oil-wet formation.
12. Nitrogen (N_2) is recommended if it is a low pressure well with xanthan or starch present.

TABLE 17 – A LIST OF CHEMICAL RULES GOVERNING MAIN TREATMENT FLUID RECOMMENDATIONS IN THE ACID ADVISER

1. If carbonate or sandstone is in the well system, HCl is recommended in the main stage.
2. HF is recommended for all sandstone formations.
3. All KCl is turned off for all HF treatments. NH_4Cl is recommended instead.
4. Organic acid is recommended if it is a high temperature carbonate well.
5. Corrosion inhibitor is recommended if an acid is recommended.
6. Corrosion inhibitor intensifier is recommended if it is a high temperature well.
7. Foaming agent is recommended if it is a horizontal well.
8. H_2S scavenger is recommended if H_2S or SRBs are present in the well system.
9. Chelating agents are recommended if the well is a high temperature carbonate.
10. NH_4Cl is recommended with clay swelling sandstone formations.
11. Clay stabilizer is recommended with a clay mobile sandstone formation.
12. Biocide and NO_3 are recommended if there is a known SRB problem.
13. It is recommended to decrease the corrosion inhibitor and corrosion inhibitor intensifier loadings if it is a hot well and a long job.
14. Alkaline pH is recommended if chelating agents are being used.
15. Nitrogen (N_2) is recommended if it is a low pressure well with xanthan or starch present.
16. Alpha-amylose is recommended if there is starch in the well.
17. Enzymes are recommended if there is xanthan gum in the well system.

TABLE 18 – A LIST OF CHEMICAL RULES GOVERNING POST-FLUSH FLUID RECOMMENDATIONS IN THE ACID ADVISER
1. Post-flush diesel is recommended if the formation should be oil-wet after treatment.   2. Post-flush mutual solvent is recommended if the formation should be water-wet after treatment.   3. Post-flush KCl or KCl-substitute is recommended if the sandstone formation has swelling clays.   4. Clay stabilizer is recommended in the post-flush for sandstone formations with known fines migration problems.   5. Post-flush foaming agent is recommended if it was pumped in the main stage.   6. Biocide and NO_3 are recommended if there is a known SRB problem.   7. Nitrogen (N_2) is recommended if it is a low pressure well with xanthan or starch present.

Creating a Treatment Summary, the Report_Click() Sub-Routine

The VBA source code controlling the Acid Adviser's Report_Click() sub-routine is very long, comprising over 70 pages if copied and pasted into a Microsoft Word document. While long, the sub-routine only accomplishes three basic tasks: (1) it records the well system attributes, Acid Adviser inputs; (2) it records the formation damage concerns and fluid recommendations, Acid Adviser outputs; and (3) it provides typical working concentrations for the chemical additives recommended. To accomplish the first and second tasks the code runs through a series of If-Then statements checking to see if each button is 'on' or 'off.' If it is 'on,' then the code records a statement to the Treatment Summary Word file. See **Figure 15** for an example of a series of If-Then statements found in the Report_Click() sub-routine.

```
If Application.ActiveSheet.Shapes("Carbonate").Fill.ForeColor.RGB = ButtonOnGreen Then
    .TypeText Text:="Carbonate Rock"
    .TypeParagraph
    i = 1
End If

If ActiveSheet.Shapes("PotassicSS").Fill.ForeColor.RGB = ButtonOnGreen Then
    .TypeText Text:="Potassium Rich Sandstone"
    .TypeParagraph
    i = 1
End If

If ActiveSheet.Shapes("IronSS").Fill.ForeColor.RGB = ButtonOnGreen Then
    .TypeText Text:="Iron Rich Sandstone"
    .TypeParagraph
    i = 1
End If

If ActiveSheet.Shapes("MobileSS").Fill.ForeColor.RGB = ButtonOnGreen Then
    .TypeText Text:="Sandstone with Mobilizing Clays"
    .TypeParagraph
    i = 1
End If
```

Fig. 15— Four If-Then statements from the VBA source code of the Report_Click() sub-routine, a portion of the Acid Adviser. The first If-Then statement tests to see if the Carbonate button is 'on.' If it is, then the phrase "Carbonate Rock" is recorded in the Treatment Summary document.

The Report_Click() sub-routine also records the typical working concentration of each fluid recommended. Much like the first and second tasks above, the typical working concentrations are only listed in the Treatment Summary if that fluid is recommended. The Report_Click() sub-routine checks the state of each fluid additive button and then records the working concentration. See **Figure 16** for an example of VBA source code controlling this portion of the Report_Click() sub-routine.

```
If ActiveSheet.Shapes("Post_MutualSolvent").Fill.ForeColor.RGB = ButtonOnGreen Then
    .TypeText Text:="Mutual Solvent: %5 is a typical working concentration."
    .ParagraphFormat.LeftIndent = InchesToPoints(1.5)
    .TypeText Text:="There is no advantage to running the concentration over 10%."
    .TypeParagraph
    .ParagraphFormat.LeftIndent = InchesToPoints(1)
    i = 1
End If
```

Fig. 16— One If-Then statements from the VBA source code of the Report_Click() sub-routine, a portion of the Acid Adviser. This If-Then statement tests to see if mutual solvent is recommended in the post-flush stage of the treatment. If it is, then the phrases "Mutual Solvent: 5% is a typical working concentration." And "There is no advantage to running the concentration over 10%." is recorded in the Treatment Summary document.

CHAPTER VIII

CREATING THE SANDSTONE SIMULATOR USING VISUAL BASIC FOR

APPLICATIONS (VBA)

In addition to the Acid Adviser, The Virtual Lab also includes the Sandstone

Simulator. The simulator is a numerical model meant to assist an engineer in designing a

matrix treatment of sandstone formations by showing how a mud acid treatment changes

skin, rate and permeability in a formation of a given mineralogy. The simulator itself is

written in the FORTRAN programming language while the interface is written in VBA.

By having the simulator accessible through an Excel-based interface, a design engineer

only needs be familiar with Excel to use it. The engineer must also ensure the Virtual

Lab Excel file as well as the FORTRAN-based executable files are both in the same file

directory. Otherwise the program will not work. **Figure 17** is a screen capture of the

Sandstone Simulator interface while **Figures 18-20** are close ups.
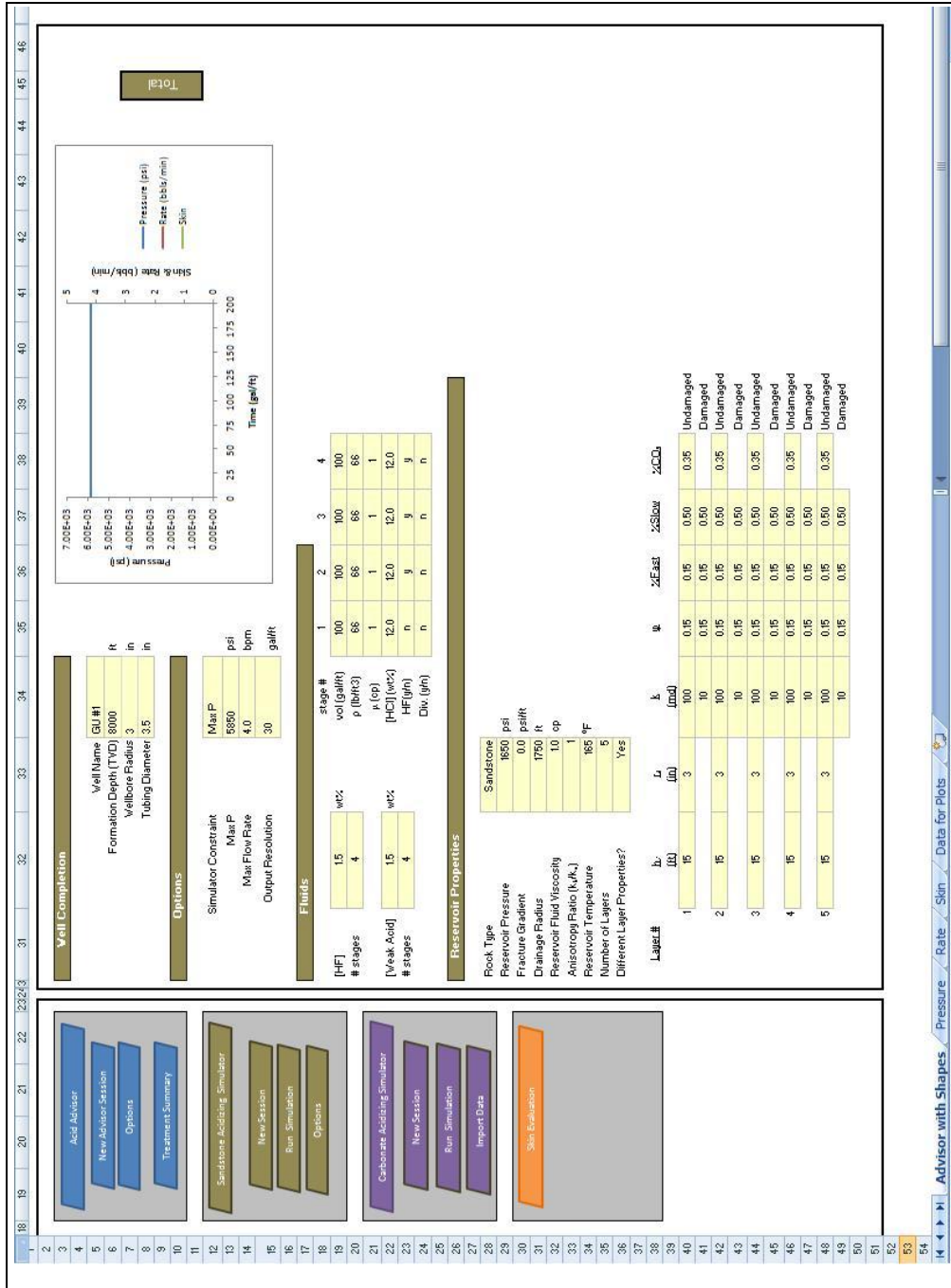
Figure 17—A screen capture of The Virtual Lab Sandstone Simulator. All yellow cells are input parameters. And the global controls for the simulator are brown buttons to the left. Output values are displayed in the chart to the upper right.

Fig. 18— A screen capture of some of the input cells for the Virtual Lab Sandstone Simulator.
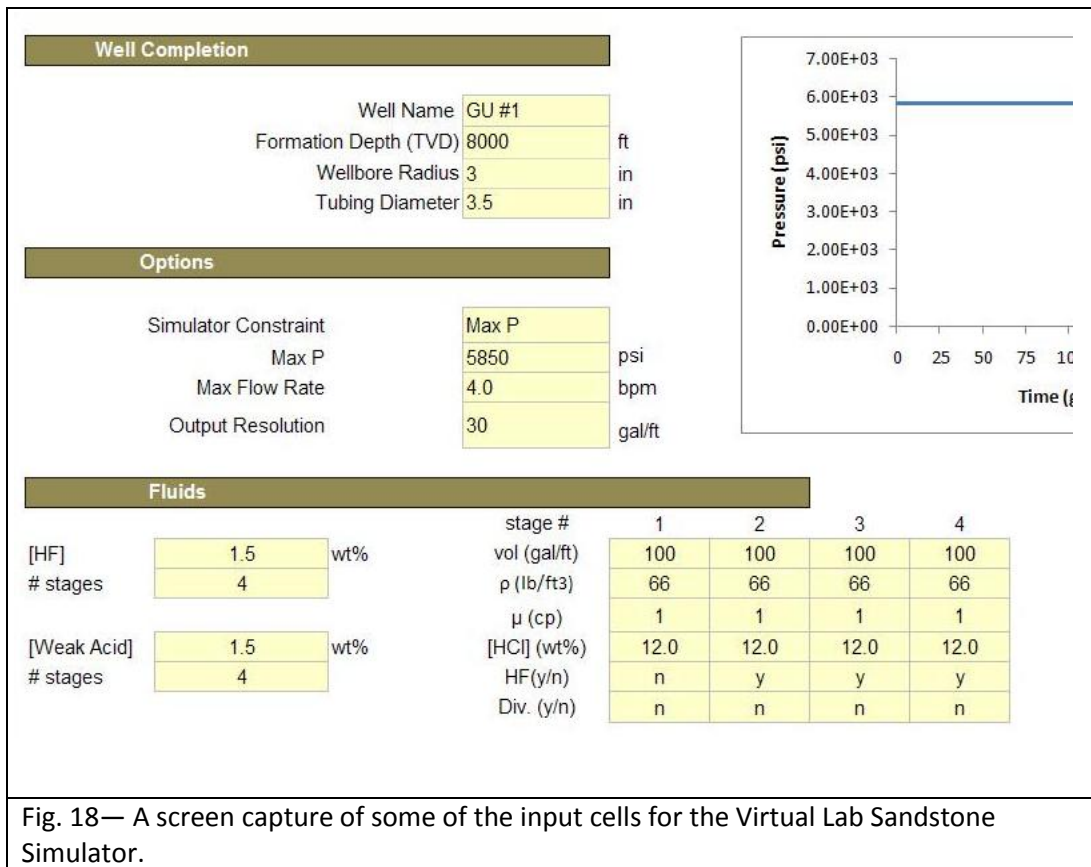
Reservoir Properties							
Rock Type	Sandstone						
Reservoir Pressure	1650 psi						
Fracture Gradient	0.0 psi/ft						
Drainage Radius	1750 ft						
Reservoir Fluid Viscosity	1.0 cp						
Anisotropy Ratio (k_h/k_v)	1						
Reservoir Temperature	165 °F						
Number of Layers	5						
Different Layer Properties?	Yes						

Layer #	h_i (ft)	r_d (in)	k (md)	φ	%Fast	%Slow	%CO₃	
1	15	3	100	0.15	0.15	0.50	0.35	Undamaged
			10	0.15	0.15	0.50		Damaged
2	15	3	100	0.15	0.15	0.50	0.35	Undamaged
			10	0.15	0.15	0.50		Damaged
3	15	3	100	0.15	0.15	0.50	0.35	Undamaged
			10	0.15	0.15	0.50		Damaged
4	15	3	100	0.15	0.15	0.50	0.35	Undamaged
			10	0.15	0.15	0.50		Damaged
5	15	3	100	0.15	0.15	0.50	0.35	Undamaged
			10	0.15	0.15	0.50		Damaged

Fig. 19— A screen capture of some of the input cells for the Virtual Lab Sandstone Simulator.

Figure 20—A screen capture of The Virtual Lab Sandstone Simulator chart. Rate, pressure and skin are all displayed on the chart. And the chart can display any of the layers or the overall values for the well.
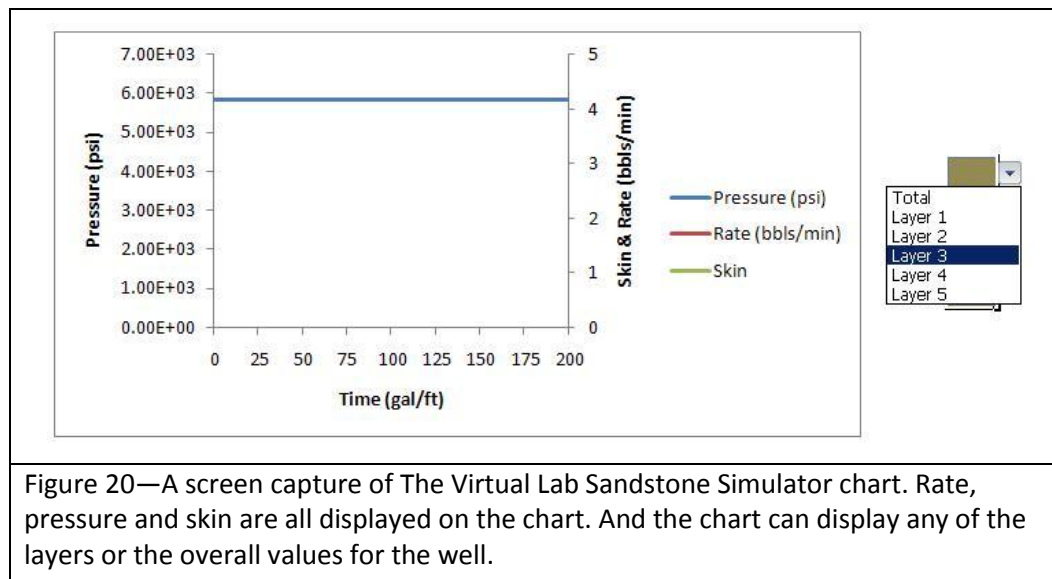
The source code controlling the simulator interface is made of eight sub-routines, six of which run each time the simulator is executed. The other two run when global controls for the simulator are accessed. See **Table 19** for a list of sub-routines controlling the simulator interface during simulation and **Figure 21** for a diagram of the flow of their control.

TABLE 19 – SUB-ROUTINES OF THE VIRTUAL LAB SANDSTONE SIMULATOR	
Sub-Routine Name	Inputs
Sub RunSandstone_Click()	None
Sub StartUTAcid()	None
Sub ImportPressureData_Click()	None
Sub ImportRateData_Click()	None
Sub ImportSkinData_Click()	None
Sub CreateSandstoneChart()	NumberofLayers, data type Integer

Fig. 21— A diagram of the flow of control of the Virtual Lab Sandstone Simulator. When a user clicks the 'Run Simulation' button RunSandstone_Click() is executed, creating INPUT.DAT. Then StartUTAcid() runs, executing the ROTRAN-based executable file. Then ImportPressureData_Click() is executed. Part of ImportPressureData_Click() calls the sub-routines ImportRate_Data_Click() and ImportSkinData_Click() and once they are finished, CreateSandstoneChart() is executed. The final sub-routine requires an input variable, NumberofLayers, which is of data type Integer.

The RunSandstone_Click() Sub-Routine

When an engineer wants to use the simulator, first they need to enter all input values into the interface. Once finished, the engineer will then need to click the 'Run Simulation' button in the Sandstone Simulator global controls, which appear as brown buttons on the left hand side of the interface. See **Figure 22** for a screen capture of the 'Run Simulation' button. The first sub-routine executed is RunSandstone_Click(), which requires to variable inputs. This sub-routine creates INPUT.DAT, the file required for

the FORTRAN-based executable file; writes values to INPUT.DAT; calls

StartUTAcid(), which runs the FORTRAN-based executable file; and then calls

ImportPressureData_Click().

Fig. 22— A screen capture of the global controls for the Virtual Lab Sandstone Simulator. Clicking 'Sandstone Acidizing Simulator' will expand or shrink the simulator interface. Clicking 'New Session' will default all input values. 'Run Simulation' creates INPUT.DAT using the values entered in the interface and runs the FORTRAN-based executable file. 'Options' allows a user to configure the interface, including some chart parameters.

The SandstoneAcidizing() Sub-Routine

The SandstoneAcidizing() sub-routine serves two purposes: (1) execute the

utacidc.exe file, and (2) execute the utacidc.exe file after the INPUT.DAT file is

complete. If the executable file is run before the input file is completely written,

erroneous results will occur or the program will return an error. The VBA code

controlling the execution of the FORTRAN-based executable file uses the Shell feature

of VBA, as can be seen by the source code, see **Figure 23**. If a programmer wanted to

change the path locating the executable file, this is the sub-routine that should be altered.

```
Sub StartUTAcid()

Dim Fortran As String
    Fortran = ActiveWorkbook.Path & "\utacidc.exe"
Dim rt As Long

    ChDir (ActiveWorkbook.Path)
    rt = Shell(Fortran, vbNormalFocus)

    If Err <> 0 Then
        MsgBox "Cannont start " & Fortran, vbCritical, "Error"
    End If

End Sub
```

Fig. 23— A screen capture of the SandstoneAcidizing() VBA source code, in its entirety.

When run, the FORTRAN-based executable file only looks for an input file

named 'INPUT.DAT,' performs calculations based on its contents, and then prints

values to a series of output files. In other words, the Excel interface must create an input

file with correct values; run the executable FORTRAN file; and then display the

generated output. The input and executable files need to be in the same directory to run

and the output files will be created after execution. See **Table 20** for a list of all

variables required for the executable file to run properly and **Table 21** for a list of output

files created once run and a description of their contents.

TABLE 20 – A LIST OF VARIABLES REQUIRED BY THE FORTRAN-BASED EXECUTABLE FILE	
Variable Name	Units or Values
imod	2
Wellbore Radius	Inches
Re	Feet
Pr	Psi
Reservoir Temperature	°F
Tubing Depth	Feet
Depth	Feet
Measured Depth	Feet
Fracture Gradient	Psi/ft
Anisotropy Ratio	Unitless
Ipor	1
Exponent	3
Number of Layers	Unitless integer
Thickness of Each Layer	Feet
Damage Radius	Inches
Original Permeability	Unitless, between 0 and 1
Damaged Permeability	Unitless, between 0 and 1
Original Porosity	Unitless, between 0 and 1
Damaged Porosity	Unitless, between 0 and 1
Carbonate Volume Fraction	Percent, between 0 and 1
Fast-Reacting, Original	Percent, between 0 and 1
Fast-Reacting, Damaged	Percent, between 0 and 1
Slow-Reacting, Original	Percent, between 0 and 1
Slow-Reacting, Damaged	Percent, between 0 and 1
Concentration of HF	Percent, positive value
Filter Cake Resistance	N/A
Acid Viscosity	Cp
Number of Injection Stages	Unitless, Integer
Volume of Each Stage	Gal/ft
Density of Each Stage	Lb/ft^3
Viscosity of Injected Fluid	Cp
HCl Concentration	Weight percent
Flag for HF	0 or 1
Flag for Diverter	0 or 1
Constrain for the Flow	0 or 1
Maximum Pressure	Positive integer
Print Frequency	Whole number, gallons

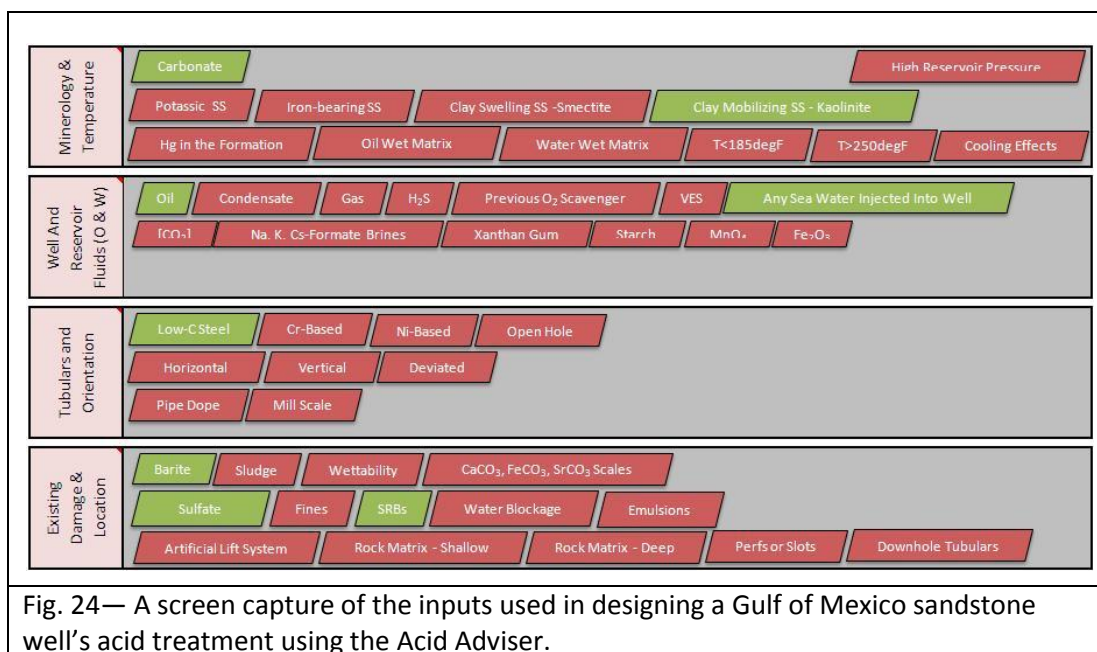| TABLE 21 – A LIST OF FILES CREATED BY THE FORTRAN-BASED EXECUTABLE FILE	
File Name	Content
OUTPUT.DAT	All outputs generated by the simulator
PERM.D	Permeability, as a function of space and time
Pressure.D	Pressure, as function of time and layer
PROFILE.D	Dimensionless mineral and acid concentrations as a function of time and space
RATE.D	Rate, as a function of time and layer
SKIN.D	Skin, as a function of time and layer, excluding viscous skin
TOTSKIN.D	Total skin, as a function of time and layer
VISKIN.D	Viscous skin, as a function of time and layer
Check.D	N/A
Interface.D	N/A
Prestest.D	N/A

Importing Simulator-Generated Pressure, Rate, and Skin Data

Once the simulator has run, several new files will appear in the active workbook file path. The Sandstone Simulator then imports rate, skin and pressure data from their prospective files.

CHAPTER IX

ACID ADVISOR EXAMPLES

The first example below shows how the Virtual Lab's Acid Adviser can assist a
production engineer design an acid matrix treatment for an off shore sandstone oil
producer.

Fig. 24— A screen capture of the inputs used in designing a Gulf of Mexico sandstone
well's acid treatment using the Acid Adviser.

This hypothetical well system is made of components often found in an off-shore
sandstone oil producer: a formation with calcite and kaolinite, a mobile sandstone clay;

reservoir fluids that include sea water and oil; low-carbon steel well tubulars; and has

known issues sulfate scaling and sulfur reducing bacteria. See **Figure 24**. Moreover, this

well was drilling with drilling mud containing barite, and though it was acidized after

drilling, there is always a concern of an incomplete removal barite from the formation,

so that input parameter is highlighted as well. **Figure 25** shows the outputs generated

from the Acid Adviser.

Fig. 25— A screen capture of the outputs used in designing a Gulf of Mexico sandstone well's acid treatment using the Acid Adviser.
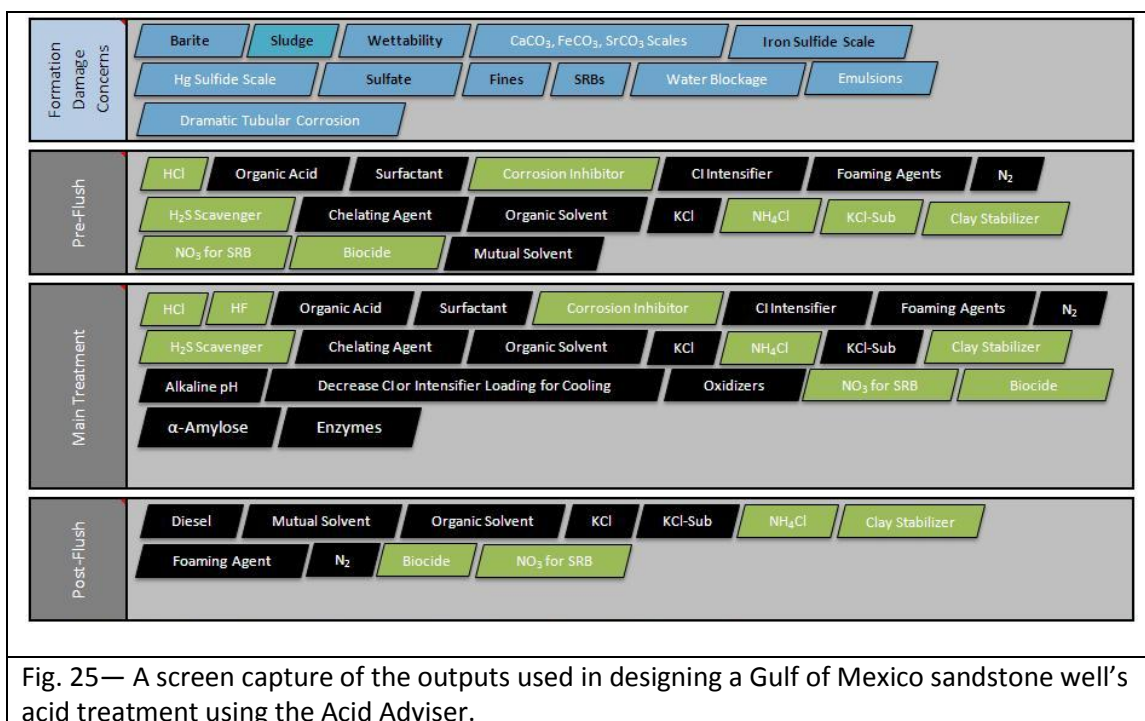
First, the Acid Adviser highlights future formation concerns in the blue section of figure

25: barite, sludge, wettability, sulfate, fines and SRBs. Concerns for barite formation

damage are highlighted because even though stimulation can help improve skin factors associated with the chemical damage caused by barite invasion from drilling mud, the chemical damage is never fully removed. Second, since the well is currently damaged with formation fines, sulfate scaling and bacteria, the Adviser highlights that these are still concerns after the treatment. Matrix treatments cannot eliminate these concerns. In fact, they can only temporarily stimulate, in an attempt to overcome the negative effects of these types of formation damage. Remember that sulfate scales are not soluble with acid. Wettability is highlighted as a formation damage concern because the stimulation of the well requires the use of acid and thus, corrosion inhibitor. And corrosion inhibitor can cause water-wet sandstone formation to become oil-wet. And lastly, any acid treatment of a formation that is accessed through low-carbon steel tubulars should be concerned about damage caused from iron (III) ions.

In response to these concerns the Adviser recommends a particular suite of chemicals for an acid treatment in this well. The following chemicals are recommended in the pre-flush: HCl to eliminate any calcite; biocide or nitrate for the treatment of sulfate reducing bacteria; a corrosion inhibitor to protect well tubulars from the HCl; an H_2S scavenger to decrease the amount of biogenic H_2S present from the bacteria; and an additive for clay control such as ammonium chloride, KCl substitute or a cationic surfactant which will help with clay stabilization. Additional testing would be required to determine which kind of clay control should be used, as the particulars are formation specific. The scavenger will help decrease the risk of iron sulfide formation. The iron

would be from unavoidable well tubular corrosion while the sulfur would be from the bacteria.

Since the risk of formation damage from FeS, clay mobilization and bacteria exist throughout the treatment, the related chemicals are also recommended in the main stage. Moreover, HF is included, as that is the principal chemical required to stimulate a sandstone reservoir. It should be noted that HF should only be applied to wells that contain less than 10% calcite before a pre-flush. Otherwise some calcite will be left over and will react with HF to form an insoluble CaF.

The post flush fluids recommended address the ongoing concerns with bacteria and clay mobilization.

Note that the Adviser does not recommend a scale inhibitor. The principle behind this recommendation is that scale inhibitor is an ineffective way to control barium sulfate scaling in off shore wells as there is simply too much sulfate in any sea water injected. Instead, any sea water should go through extensive processing to remove the sulfate. Some operators choose to use rig-mounted reverse osmosis systems. If such a system cannot be used, or cannot get the sulfate concentration under 50 ppm, then the post-flush should include a scale inhibitor. If the scale problems are so bad as to prevent pumping into the well, then the mechanical removal of the scale is suggested as barium sulfate is not soluble in acid solutions. Moreover, if too much corrosion inhibitor is pumped into the well and the wettability is thought to have changed, then mutual solvent should be pumped to re-establish water-wet conditions.

The second example shows the recommendations and concerns when acidizing a sour gas well, found in a carbonate reservoir, using low-carbon steel tubulars. This particular hypothetical well is known to have mercury in the formation, so that input is highlighted as well. See **Figure 26.**

Fig. 26— A screen capture of the inputs used in designing a Middle East carbonate gas well's acid treatment using the Acid Adviser.

Fig. 27— A screen capture of the outputs for a hypothetical Middle East carbonate gas well acid treatment using the Acid Adviser.
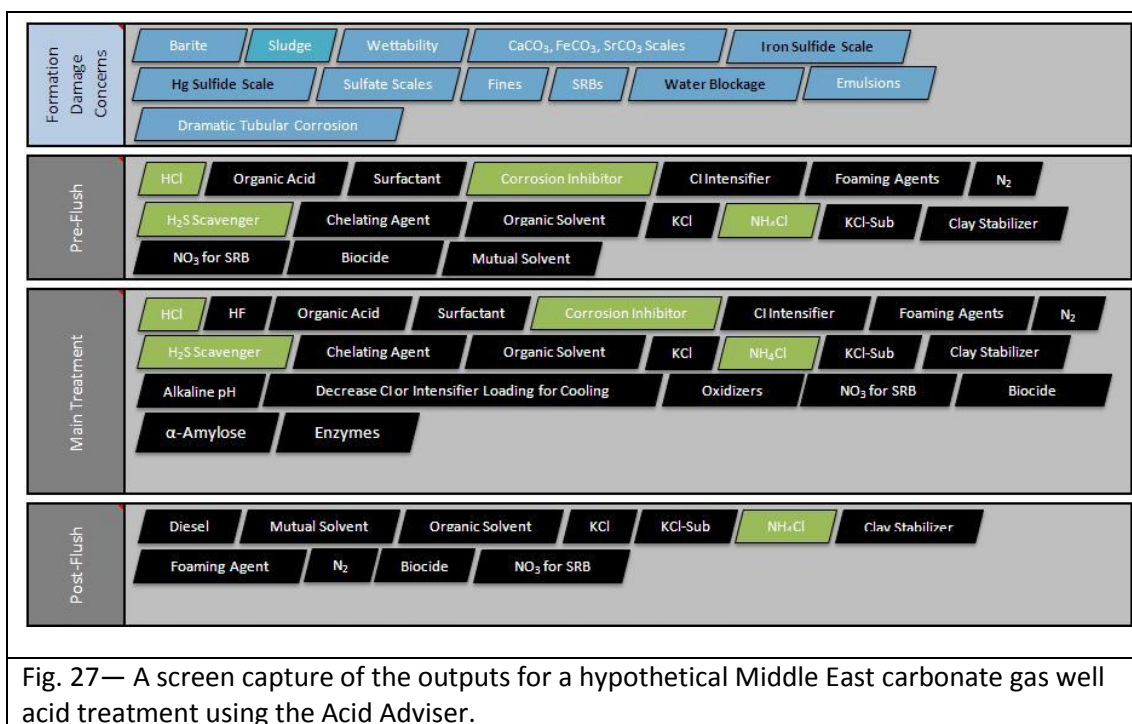
The Adviser highlights three main concerns for formation damage: mercury sulfide scaling, iron sulfide scaling and water blockage. See **Figure 27**. The mercury sulfide scale is a relatively rare scale that can form when mercury is present in the formation as well as a sulfur source. Since this is a sour well with mercury in the formation, this concern is highlighted. Second, iron sulfide is highlighted because of the risk of iron sulfide precipitation forming with the reaction of iron ions and H2S. The iron ions would be formed after a reaction of acid and well tubulars. Moreover, since this is a gas well any injection of liquids runs the risk of causing a decrease in the relative permeability to gas, also known as water blocking.

In response to these concerns, and the initial well conditions, the following fluids are recommended: HCl; a corrosion inhibitor; an H_2S scavenger; and ammonium chloride. The HCl is used to stimulate the carbonate formation, creating wormholes. And the corrosion inhibitor protects the tubulars. The H_2S scavenger plays two roles in this treatment, and is particularly important in the pre-flush. First, it will decrease the H_2S available for the creation of any sulfide scale, iron or mercury. Secondly, additional scavenger should be include in the pre-flush as to act as a squeeze treatment of hydrogen sulfide beyond the stimulated region. This not only help minimize the creation of new formation damage by preventing iron sulfide formation, but also helps prevent any future formation damage from mercury sulfide. The ammonium chloride recommendation is optional, as its use depends on formation mineralogy. Some carbonates contain swelling clays that can be controlled using chloride salts.

CHAPTER X

CONCLUSIONS

When McLeod published his tables over two decades ago only some mechanisms for formation damage and remediation were well understood. But through practical experience and industry-wide research efforts there is now a clearer understanding of many more damaging mechanisms. As such, the Virtual Lab software package attempts to convey the appropriate qualitative mechanistic information and quantitative tools to assist the practicing engineer in proper acid and additive selection; acid injection rates; and treatment concentrations given well parameters. This stimulation advice is communicated through a graphical format for ease of use.

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Research Assistant, 2009-current
- Supervisors: Assistant Dept. Head, Dr. Hill, Dr. Zhu, Dr. Hisham Nasr-El-Din.
- Research focus: Production Engineering.

EXCO Resources – Dallas, TX
Intern, Summer 2009
- Participated in operations ─ coiled tubing, workover, wireline and fracturing.
- Presented costs and benefits of possible Vapor Recovery for Danville field facility.

Cudd Energy Service – Kilgore, TX
Scientist, 2008-2009
- Responsible for all water, fluid and sand analyses.
- Directly monitored all cross linked jobs for Quality Control.
- Developed zirconate fluid system to achieve cross linked fluid stability over 330°F.

Baker Atlas – Tyler, TX
Open Hole Field Engineer, 2007-2008
- Acquired data using Atlas' density, neutron, induction, minilog and acoustic tools.
- Created presentations, managed small crew and led operations at the truck level.
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Education & Professional Experience

M.S. Petroleum Engineering, May 2011
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- *Presented research on pressure transient response of shale gas reservoirs*

B.S. Genetics, May 2004
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- *Senior Merit Award – a top student (of ~6,000) in College of Ag and Life Science*
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