POTENTIAL OF BARITE-WEIGHTED EPOXY SYSTEMS TO PLUG WELLS IN THE GULF OF MEXICO

A Thesis

by

ZHUO GAO

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

December 2011

Major Subject: Petroleum Engineering

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Approved by:

Chair of Committee,	Robert Lane
Committee Members,	Jerome Schubert
	Yuefeng Sun
Head of Department,	Steve Holditch

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ABSTRACT

Potential of Barite-Weighted Epoxy Systems to Plug Wells in the Gulf of Mexico.

(December 2011)

Zhuo Gao, B.S., China University of Petroleum (East China), P.R.China

Chair of Advisory Committee: Dr. Robert Lane

In the past ten years, there have been 194 hurricane-damaged platforms in the Gulf of Mexico (GOM), each with many wells that have not been permanently abandonment. This could lead to disastrous environmental consequence. The wells where their platforms were destroyed by hurricanes cannot be abandoned by conventional methods. Our research showed that barite-weighted epoxy material could be potentially used for well abandonment for those wells in GOM. Shear bond strength tests showed that between two candidates epoxy systems—the bisphenol A system and the bisphenol F system, the latter was less sensitive to barite weighting material. The shear bond strength of besphenol A system was deteriorated as barite increased, while bisphenol F system showed slightly increasing trend when barite was added. The minimum bond strength given by bisphenol A system appears around 68 wt% of barite, which is around 1290 psi. The maximum value of 2200 psi comes at 0 wt% of barite. And the bisphenol F system can stand a minimum of 1010 psi bond strength at 0 wt% of barite, and a maximum of 1160 psi of bond strength with 70 wt% of barite. Moreover, mixing with seawater did influence the shear bond strength between epoxy system and low-carbon steel. The influence that seawater has on the F system is less than that of the A system. The time that the epoxy system needs to fully develop the bond is far longer than curing time determined in our parallel research. Bond strength is lower in both seawater environment and at high temperature.

DEDICATION

I dedicate this thesis to my family and friends, especially

to Dad and Mom for instilling the importance of hard work and higher education;

to Yi for her patience and understanding—may you also be motivated and encouraged to reach your dreams.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Lane, and my committee members, Dr. Schubert, Dr. Sun, for their guidance and support throughout the course of this research.

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Thanks also to my colleagues, for helping me with the experimental setup and running the experiments.

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Finally, thanks to my parents for their encouragement and love.

NOMENCLATURE

HTHP	High Temperature High Pressure
BOEMRE	the Bureau of Ocean Energy Management, Regulation and Enforcement
MMS	Minerals Management Service
GOM	Gulf of Mexico
API	American Petroleum Institute
DOGGR	California Department of Conservation Division of Oil, Gas and Geothermal Resources
ASTM	American Society for Testing and Materials
FEM	Finite Element Method
AAF	Aqua-Advanced Fabric
EEW	Epoxide Equivalent Weight
AHEW	Amine Hydrogen Equivalent Weight
PHR	Per 100 Parts Resin
BPA	Bisphenol A Type Resin
BPF	Bisphenol F Type Resin
ROR	Reduced-bond-strength/Original-bond-strength Ratio

TABLE OF CONTENTS

Page

CHAPTER

CHAPTER Page

LIST OF FIGURES

Page

Page

LIST OF TABLES

CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

In the GOM, approximately 180 offshore platforms were damaged and destroyed by hurricanes in the past several years according to the documents released by the Bureau of Ocean Energy Management, Regulation and Enforcement (BOEMRE). The major hurricanes that passed through the Gulf of Mexico during the last dozen years are Andrew in 1992, Lili in 2002, Ivan in 2004, Katrina and Rita in 2005, and Gustav and Ike in 2008. **Table 1** shows the statistics for hurricanes damaged or destroyed platforms released by BOEMRE in a report of 2006 after hurricane Ivan. From **Fig. 1,** we can see that the major hurricanes pass through dense offshore locations, which leads to the disaster of our offshore industry.

This thesis follows the style of *Society of Petroleum Engineering*.

Table 1–HISTORICAL DAMAGE TO OFFSHORE FIXED PLATFORMS FROM HURRICANES IN GOM (BOEMRE, 2010).

No.	Hurricane	Year	Structures Destroyed**	Industry Response or Source
1	Grand Isle	1948	2*	Limited number of platforms in service
2	Carla	1961	3*	
3	Hilda	1964	14*	Several operators start to use a 100 year return period design wave
4	Betsy	1965	8*	
5	Camille	1969	3*	1st ed. API RP2A for fixed platform design
6	Carmen	1974	2*	
7	Frederic	1979	3*	Wave load recipe provided in RP2A
8	Juan	1985	3*	Assess-Inspect-Maintain (AIM) Joint Industry Projects for existing platforms
9	Andrew	1992	28 / 47 / 75	PMB, Andrew JIP, 1996.
10	Lili	2002	8 / 0 /8	Puskar, et.al., OTC 16802, 2004.
11	Ivan	2004	6 /1 / 7	MMS TAR No. 549, Energo, 2006
12	Katrina	2005	45 / 0 / 45	MMS TAR No. 578, Energo, 2007.
13	Rita	2005	56 / 18 / 74	MMS TAR No. 578, Energo, 2007
14	Gustav	2008	1 /0 / 1	MMS New Release November 2008
15	Ike	2008	50 / 9 / 59	MMS News Release November 2008
Total Historical GOM			232 / 75 / 307	

* Platform failures based upon published reports at the time (no data on caissons). Additional failures may have occurred but not reported in literature.

** Data shown as Platforms / Caissons / Total

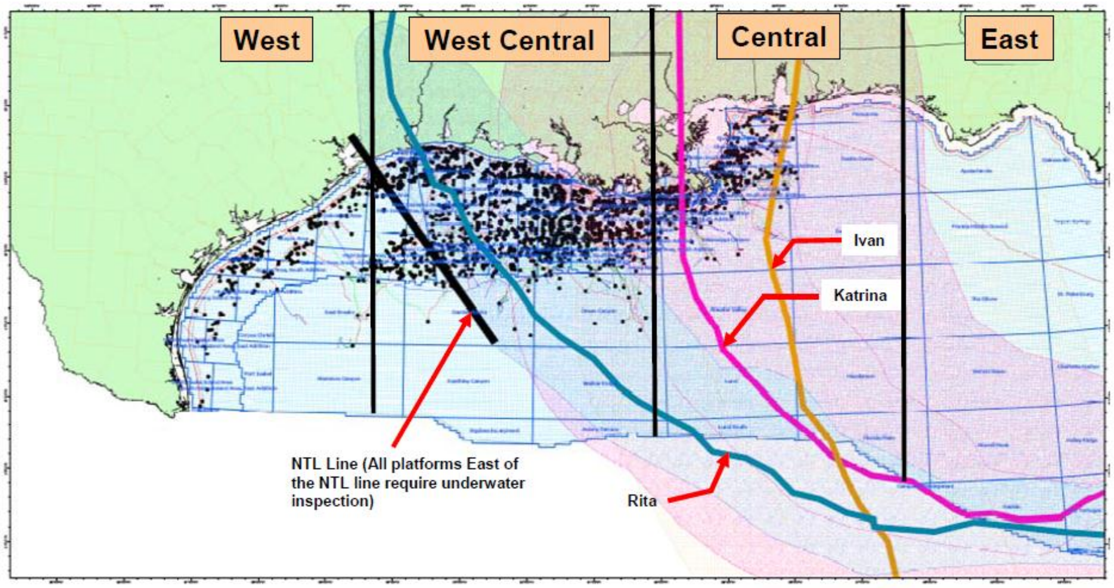


Fig. 1–Path of hurricanes Katrina and Rita and the Gulf of Mexico offshore infrastructure location (BOEMRE, 2007)

The report released by MMS (the former name of BOEMRE) in 2006 said that there were 28 fixed platforms destroyed by Andrew of 1992, 7 by Lili of 2002, and 7 by Ivan hurricane in 2004 (BOEMRE, 2006).

In the report of 2007 shows there are a total of 116 destroyed fixed platforms from Katrina and Rita in 2005 and one floating platform (BOEMRE, 2007). The dots in **Fig. 2** show the location of destroyed platforms after Katrina and Rita. Most of these 116 platforms were either completely toppled to the seafloor with no structure visible above the waterline, or were so severely damaged that it was obvious the structure was destroyed by the hurricanes and could no longer carry out its purpose and had to be removed. Moreover, **Fig. 3** shows how far the platform was moved by hurricanes in sonar image. And **Fig. 4** was a underwater picture of toppled platform. **Fig. 5** shows how the hurricane destroyed platform look like in Gulf of Mexico after Katrina and Rita.

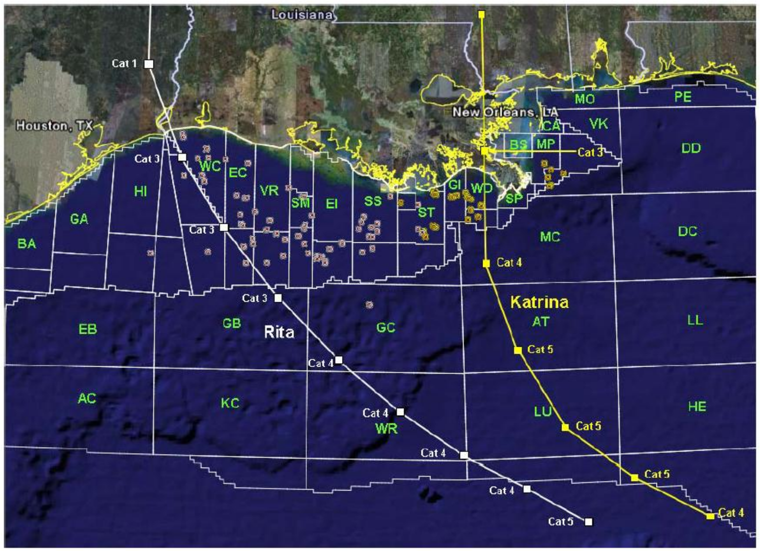


Fig. 2–Location of destroyed platforms in Gulf of Mexico compared to path of hurricane Katrina and Rita (BOEMRE, 2007)

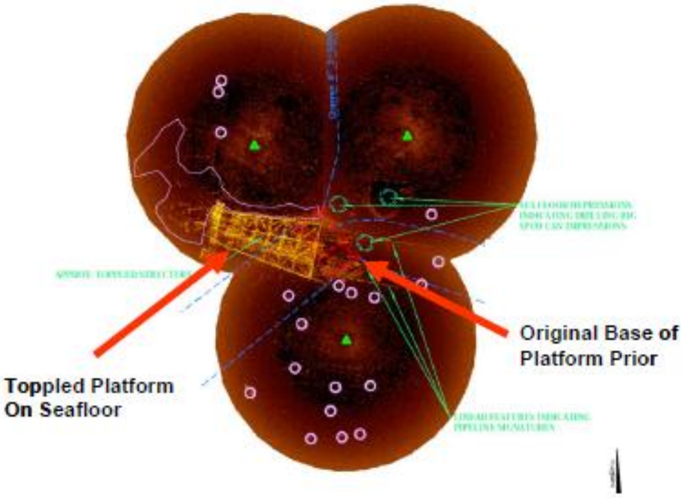


Fig. 3–Sonar image of the toppled platform in the west delta area after Katrina and Rita (BOEMRE, 2007).

Fig. 4–Underwater photo of a toppled platform in the Eugene Island Area (BOEMRE, 2007).

Fig. 5–Destroyed platform in the South Timbalier region after Katrina and Rita in 2005 (BOEMRE, 2007).

Another report officially released in 2010 by BOEMRE presents that there were a total of 60 destroyed fixed platforms in Gustav and Ike in 2008 (BOEMRE, 2010). No floating platforms were reported destroyed in the report. **Fig. 6** shows both the path of hurricanes Gustav and Ike, and the locations of destroyed platforms, which are marked by red dots. **Fig. 7** shows the typical appearance of a hurricane damaged platform after Gustav and Ike.

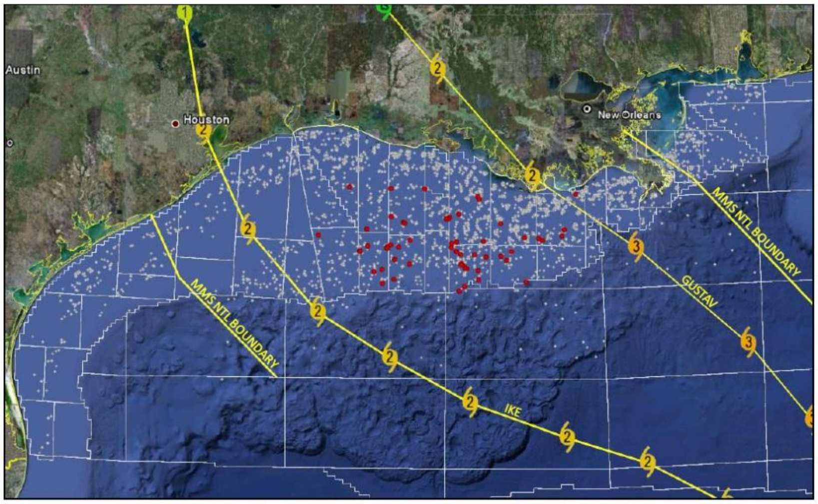


Fig. 6–Location of destroyed platforms compared to path of hurricanes. The red dots indicate destroyed platforms (BOEMRE, 2010).

Fig. 7–Destroyed platform in the Eugene Island Area from Gustav and Ike in 2008 (BOEMRE, 2010).

In cases where platforms have been completely destroyed and toppled, the wells can no longer safely produce oil or gas, and/or have become an environmental hazard. Additionally, such wells cannot be plugged and abandoned by conventional methods. Instead a subsea intersection well may have to be drilled to provide access to the wellbore. Depending on the intersection and the condition of the target well, it may not be possible to circulate or pump cement all the way down to the wellbore. In these cases, a plugging material needs to be spotted at the intersection of the target well, and allowed to fall through the wellbore, and settle at the target plugging zone, which includes annulus and across production interval, and seal the well permanently. **Fig. 8** illustrates a hurricane destroyed well in the Gulf of Mexico. The shadow area in red is the target plugging zone that we proposed to abandon.

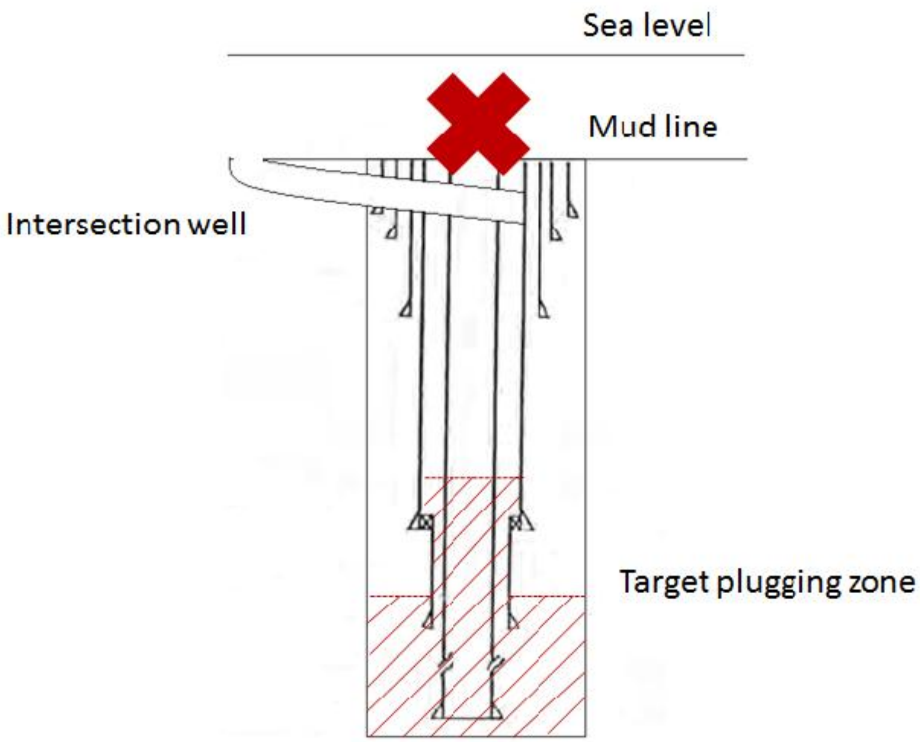


Fig. 8–Schematic of hurricane damaged offshore wellbore

The conventional methods to plug a well offshore include cement slurry plug, inflatable packer, and compressed sodium bentonite (Englehardt et al., 2001). Cement slurry plug is the most commonly used plugging and abandonment material in the oil and gas industry. However, there is a major disadvantage in using it offshore to abandon wells destroyed by hurricanes. Cement is miscibility with seawater and other brine. Such wells are often filled with seawater. Circulation system and mud are the main approach that people onshore use to avoid the contact of cement and unwanted fluid. Secondly, these offshore platforms don’t have any circulation system any more, which delivers the high viscosity cement to the spot cannot work with destroyed platform. So as long as cement is applied, mixing with seawater cannot be avoided. Last but not least, in terms of its particle based structure, the material exhibits relatively poor penetration capabilities in formations and wellbores. Most of the platforms which need to be permanently abandoned had been in service at least a couple of decades before being destroyed. Long time of soaking in the seawater undoubtedly leads to plenty of corrosion and ocean organisms along the wellbore. **Fig. 9** shows the external conductor appearance after hurricanes, which should be similar to what the interior looks like. The disadvantages of cement inhibit itself being applied in this project.

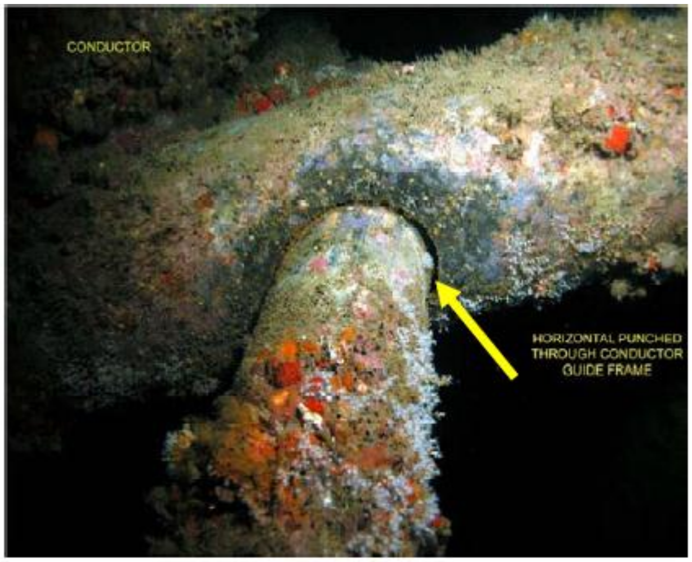


Fig. 9–A underwater picture of conductor surface (BOEMRE, 2006).

Inflatable packer is a promising technology for temporary or permanent well abandonment, which has been successfully applied in the Gulf of Mexico (Vaucher and Brooks, 2010). Basically, it is a smartly designed mechanical tool, containing rubber cover and exposed metal slats. It mostly relies on expansion of rubber cover to seal, and friction between metal slat and wellbore to locate. The literature states that it's versatile of being conveyed to the depth by threaded tubing, coil tubing, electric wire-line and slick-line or braided line. However, all tubing and wire-line conveying method can only be applied when there is direct access to the wellbore, which is not available for wells on toppled platform where risers have been severely damaged.

Another relatively new abandonment material is compressed sodium bentonite (Englehardt et al., 2001). Both research and field test shows several advantages of compressed sodium bentonite. For example, it can easily fall through the wellbore and be hydrated to form an impermeable plug in oil or gas wells; it can form a plug in seawater and be stable at high temperature; it also can be reentered by using a soft formation drilling facility. Although it can be applied as a weighting material, it is not an adhesive material. So it cannot effectively seal a wellbore. Moreover, its applications are more focusing on onshore abandonment, especially temporary abandonment. No application or research shows that it has been successfully applied in permanent offshore abandonment. In terms of these restricted conditions, conventional plug and abandonment method won't be feasible.

Our research is seeking an alternative method to plug and abandon the well in deep water and particular reservoir condition economically and feasibly. Epoxy-based material popped up in terms of its excellent performance in casing repair, sand consolidating, and well plugging. The epoxy-based material formula generally contains cross-linkable epoxy, cross-linking agent, and optional filler according to the specific scenarios. The plugging fluid's viscosity should meet the requirement of flowing from the intersection spot and the pot life should be long enough to let the fluid fall all the way down to the top of packer and across the production interval. Also, the bond strength between epoxy system and low-carbon steel should be large enough to stand the relative high temperature and pressure at wellbore.

Permanent plug and abandonment is done with the objective for the well to be sealed and isolated forever. The long-term plugging requirement is one of the principle parameters to measure the success of abandonment. Well abandonment has never received as much attention as reservoir evaluation, drilling procedure and production process. It is a crucial step in a well's life circle especially from an environmental perspective, even though it cannot bring any revenue to the industry. American Petroleum Institute (API) has generated a report entitled, "Environmental Guidance Document: Well Abandonment and Inactive Well Practices for U.S. Exploration and Production Operations". This is considered as the standard in the industry for abandoning the wells environmentally. However, this regulation mainly emphasizes on plugging unwanted zone and onshore abandonment instead of permanent abandonment. Also, their regulation was mostly generated based on cement operation. Besides the regulation of API, California Department of Conservation Division of Oil, Gas and Geothermal Resources (DOGGR), as the lead agency in oil and gas industry in California, also released the requirement of well abandonment in State of California Code of

Regulations, Title 14 Natural Resources, Division 2 Department of Conservation, Chapter 4 Development, Regulation, and Conservation of Oil and Gas Resources, Section 1723 (Harris and Adams, 2007). They have requirement in different operations, such as plugging of oil or gas zones, plugging for freshwater protection, plugging at a casing shoe or the casing stub, and surface plugging. These regulations are also concentrated on onshore abandonment. Even though in some material they mention the regulations in California give the restrictions of offshore well abandonment, it doesn't show quantities requirements and doesn't make engineering work easier either. In general, offshore abandonment is regulated by more strict requirements than that for onshore operation. Unfortunately, BOEMRE hasn't successfully established any regulation on offshore well plugging and abandonment. The strongest one that we can find so far is the one set by the North Sea (Liversidge et al., 2006). The critical criterion is that the plug should pass the test with minimum inflow pressure of 725 psi. In our project, we assume that the BOEMRE will give us the regulation as tight as that in the North Sea. So shear bond strength is the main parameter we tested in our experiment.

BOEMRE is interested in Epoxy-based material application, because it has been used around for decades as an adhesive material, and has been extensively utilized in the whole petroleum industry. The first couple of successful applications in the petroleum industry were in the 1950s. One was as a coating material (Radecke et al., 1959), the other one was as an alternative casing repair material (Kemp, 1964). It quickly won good reputation in terms of its fast reaction and low expense since then. Its first patent in casing repair was published in 1994 (Ng et al., 1994), which deal with onshore corrosive casing and plugging the thief zone. The well is located at levels in excess of about 5,000 ft, which is often exposed to high temperature, high pressure and corrosive chemicals.

In our project, the operation environment is much tougher than the one mentioned in the patent. The wells are located in deep water of the Gulf of Mexico. The depth of the wells is beyond 5,000ft, whose effective dropping depth might up to 7000ft. The temperature at the bottom of the wellbore might as high as 250 ℉. The falling trail is the casing annuli which is narrow and full of seawater and oceanic organisms attached to the wall. No fluid will be circulated in the system. The only way to abandon a deep-water well with casing completion is pouring the abandonment fluid from intersection and letting it fall through the annuli and set the target plugging zone. To guarantee the falling process, a weighting material—barite is considered to increase the weight of the epoxy system. One reason is that the density of pure epoxy system is quite close to the density of seawater. It might float on the surface or at least be near naturally buoyant instead of falling down. The other reason is that barite is most commonly used filler with low costs in the petroleum industry. Besides low viscosity, relative high specific gravity, the scenarios also require appropriate pot life, acceptable rheology and bond strength.

1.2 Literature review

Epoxy-based material has developed from the 1950s as a coating material for corrosive protection (Radecke et al., 1959). There are several applications, such as coating, casing repair and sand consolidation, whose advantages of quicker reaction and less expensive operation won reasonable success.

The first application of epoxy as a sealant material in petroleum industry was in 1979 (Cole, 1979). The paper mainly introduced an epoxy sealant-cementing system which performs adhesive and compressive strength, together with chemical resistance superior to Portland and modified Portland type cement. In their research, they tested bisphenol A type epoxy resin with silica fillers. They overcame two serious limitations of epoxy applications by adding nonreactive liquid diluent and fillers to the system. Nonreactive liquid diluent extended latitude pumping time. Inert fillers added strength and reinforcement to the set epoxy sealant allowed more exothermic control than cementing and also reduced the cost of the whole system. Laboratory work showed epoxy adhesive very well to the metal and silica surface. Moreover, the paper mentioned that bisphenol-A type epoxy resin functioned very well in the chemical resistance and bonding strength test. Laboratory tests determining chemical resistance showed that the epoxy could provide suitable protection at temperature up to 60 ℃ from exposure to oilfield brines up to 10%, hydrochloric acid solutions up to 30% and sulfuric acid solutions up to 25% and so on. The bonding strength of the epoxy material was studied in the laboratory as well, which identified that neat epoxy sealant required 3000 psi hydraulic pressure to leakage, and epoxy slurry sealant didn’t fail even beyond 500 psi hydraulic pressure added. However the operation process mentioned in the paper was still conventional one using circulation system. Even though the reservoir condition is not the same as that in our project either, at least it showed the potential being applied in our research.

The use in pipeline coating is quite mature. It also has several problems to be concerned when applying. A paper (Jensen et al., 2000) answered the question, Whether using epoxy to repair pipeline is safe when the environment is complicated and how environment affected the mechanical properties of epoxy-bonded joints for possible use in underwater pipe line repair. They carried out their lab work in testing the interfacial shear strength--three point flexure, scanning electron microscopy, optical microscopy, and X-ray photoelectron spectroscopy to determine the failure of the bonded joints. The result shows that water diffuses through the interface between epoxy and steel resulting in the weaker bond, which is concern in our project. However, the epoxy that they tested is the one without fillers, which is quite different from our formulation. Also, we got to know that surface analysis shows failure always occurs within oxide layer from their research.

One US Patent named "casing repair using a plastic resin" mentioned biophenol-A epichlorohydrin epoxy resin mixed with reactive diluents, a mono-functional glycidyl ether based alkyl groups of C8-C10, could perform rather good seal in salinity and low temperature with specific curing agent. The patent also gives some suggestion in high temperature application, which would replace curing agent from a Mannich base aliphatic polyamine to anhydride. Moreover, the operation method mentioned in the patent is dump bailer draining, which require the viscosity of the liquid not too high to flow (Ng 1994). In our research, we are looking for pourable liquid epoxy material to abandon the 7000-feet well in temperature up to 250℉. The viscosity should be low enough for flowing. The pot life should be long enough for the liquid to fall. The patent provides good reference in formulation, but improvement is still needed.

A more nearly United States Patent 7886823 filed in 2005 provides a commercial formulation over well plugging material that can be used for both down-hole mixing and applications in brines. (Boyce D Burts et al., 2011). They found the component A and B can react with each other at down-hole form the plugging without any circulation system. However, they improved cement formula to accomplish the objective instead of using epoxy-based material.

Also, another patent 7748455 from the same author showed another formula of epoxy as a plug component for well remediation. The material in the patent are EPON 862 or 863-RESIN, EPICURE 3046 low-temp hardener, EPICURE W high temp hardener, Heloxy 7-primary reactive diluent, CARDURA E10P-secondary, high-temp diluent. The formulas are presented in Table 2. In generally this patent was designed meet the requirement that the resin component and the activator component are mixed at the surface and then placed in the annulus and allowed to form into a hard impermeable mass. Preferably, epoxy system is heavier than the well fluid to allow gravity flow through the well fluid to the annulus (Boyce D Burts, 2010).

Table 2–FORMULAS OF EACH EPOXY SYSTEM IN PATENT 0133069

Formulation	Resin	Low-temp hardener	High-temp hardener	Primary reactive diluent	Secondary, high-temp diluent	Temperature Range (°F)
	EPON 862/863 (g)	EPICURE 3046 (g)	EPICURE W (g)	Heloxy 7 (g)	CARDURA E10P (g)	
1	100	17-40				50-100
2	100	20-60		20-50		70-125
3	100	10-20	10-20	20-50		125-175
4	100		17-35	0-50		175-250
5	100		15-25	30-50	0-20	250-350

A bio-geosciences paper illustrates the geophysical and geochemical characteristics of Gulf of Mexico, which supply us with the component of bottom seawater in Gulf of Mexico (Joye et al. 2005). We will carry out experiment to evaluate the influence given by seawater.

Even though there is plentiful literature of the application of epoxy-based material, we need to consider the filler effect in our project. A study was developed to see the influence of adhesive thickness and aluminum filler content on the mechanical performance of aluminum joints bonded by aluminum powder filled epoxy (Kahraman et al., 2008). They carried out the research by single-lap shear test that is standardized by American Society for Testing and Materials (ASTM) and Finite Element Method (FEM) simulation. The study showed that adhesive thickness has a negative effect on shear strength which is verified by both lab experiment and FEM. With neat epoxy with no fillers, increase of adhesive thickness from 0.03mm to 1.3mm resulted in a decrease of about 35-40% in adhesive joint sheer strength. Also the epoxy adhesive retains its adhesion strength even with as much as 50wt% addition of filler. Failure tests showed the failure mostly occurred within adhesive. The shear and Von Mises stresses for various bond thicknesses and various adhesive compositions were analyzed by FEM. Von Mises stress attains maximum at the edges and decrease away from the edges. Adverse effect of adhesive thickness increase in bond strength was observed from comparison between different thickness specimens.

Moreover, epoxy-based adhesion is always exposed to the environment of moisture, freezing and thawing, temperature, and corrosive liquid. So it is quite significant to evaluate the environmental effects on epoxy-based adhesion. The paper published in Construction and Building Material Journal shows the decrease in flexural strength of epoxy-bonded concrete prisms is directly proportional to the adsorbed water content. And corrosive environment with $MgCl_2$ or $MgSO_4$ is not significant to bond stability (Çolak et al., 2009).

A couple of papers on evaluation of material and structural performances gave us an idea to use ASTM standard to carry out our shear bond strength test (Yi et al., 2010)and (Jensen et al., 2000).Their paper shows they did compressive strength, tensile strength test, flexural strength test, thermal expansion test, hardening shrinkage test, and chemical resistance test for Aqua-Advanced Fabric Reinforced Plastic (AAF). Pull-out test showed that failure load increases as the bonded area increased.

CHAPTER II

PROBLEMS

In this project, we will focus on shear bond strength tests. Studies showed that different aspects like fillers added and environment influenced the bond strength of epoxy-bonded material (Çolak et al. 2009) and (Kahraman et al. 2008). Plenty of literature shows the potential of epoxy-base material in aquatic environment. However, so far nothing in the literature has evaluated application of the barite-weighted epoxy system to low-carbon steel with or without the presence of synthetic seawater. We will evaluate the influences of possible aspect on bond strength, such as fillers, aquatic system, and time.

Our project is to determine the shear bond strength of epoxy system as a function of

- Composition
- Filler loading
- Curing in seawater
- Bonding to low-carbon steel
- Time
- Temperature

CHAPTER III

THEORETICAL BACKGROUND

To determine the formulation, we need to consider at least two requirements. One is to be able to applied in seawater environment; the other one is that pot life should be long enough for well operations and falling process.

For the first requirement, our research focused on two most widely used commercial epoxy systems–B47 and XR40 (two commercial products offered by Royce International Company)–to carry out our evaluation tests in our research. B47 is also known as bisphenol A type resin, while XR40 is commonly known as bisphenol F type resin. In order to be able to perform in the tough seawater environment, curing agent K450 (a commercial product offered by Royce International Company) was selected. The curing agent has a successful application history in underwater conditions according to industry expert's suggestion. Also, it is non-MDA curing agent, which is more environmental benign (Norsworthy, 2001).

For the second requirement, theoretical calculations are needed to determine each component that is applied in the formula. To obtain optimal properties with epoxy curing agent and resins, the component are typically used at approximate stoichiometric levels.

Determine the epoxide equivalent weight (EEW) of resin mixture:

$$\text{EEW of mixture} = \frac{\text{total weight}}{\frac{\text{wt. A}}{\text{EEW A}} + \frac{\text{Wt. B}}{\text{EEW B}} + \frac{\text{Wt. C}}{\text{EEW C}}}$$

Determine of amine hydrogen equivalent weight (AHEW) of the curing agent mixture:

$$\text{AHEW of mixture} = \frac{\text{total weight}}{\frac{\text{wt. A}}{\text{AHEW A}} + \frac{\text{Wt. B}}{\text{AHEW B}} + \frac{\text{Wt. C}}{\text{AHEW C}}}$$

Calculate the parts by weight of curing agent per 100 parts resin (PHR) using the following equation:

$$\text{PHR of the curing agent} = \frac{\text{AHEW of Curing Agent}}{\text{EEW of Resin}} \times 100$$

The equations listed above are used to calculation the pure epoxy resin system.

CHAPTER IV

EXPERIMENT AND DISCUSSION

4.1 Comparison of two epoxy system

One of our objects is mainly to see how these two commonly used epoxy system will perform with metal material and seawater when reacting with the curing agent. The other objective is to test properties of barite-weighted epoxy systems instead of the pure epoxy system. So we mixed barite as filler in the epoxy formulation mentioned above. We added barite for bisphenol A type resin up to 72 wt%, which is around 2.1 $\mathrm{g/cm^3}$ (17.5 ppg), and for bisphenol F type resin up to 70 wt%, which is also around 2.1 $\mathrm{g/cm^3}$ (17.5 ppg).

The two formulations visually look quite similar (shown in **Fig. 10**). The recipes and physical properties of each epoxy system are tabulated in **Tables 3** and **4**, respectively. We obtained 4 to 10 micron barite powder from our drilling lab (shown in **Fig. 11**). This is also the commonly used barite in the industry.

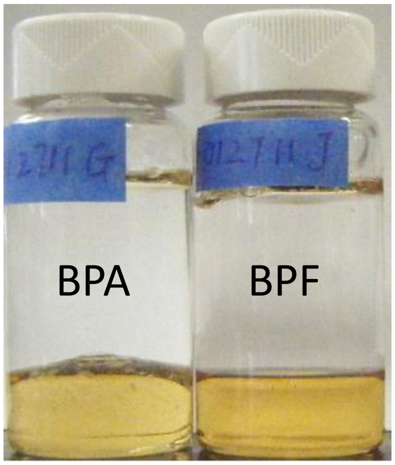


Fig. 10–The pictures of pure formulations of BPA and BPF

Fig. 11–The picture of barite powder applied in our research

Table 3–RECIPES OF EPOXY SYSTEMS

System	**Resin, g**		**Diluent, g**		**Curing agent, g**	
	Product	Amount	Product	Amount	Product	amount
A	B47*	4.7			K450	1.6
F	XR40	4.25	RA100	0.75	K450	1.9

B47* is a resin with diluent premixed in it.

Table 4–PROPERTIES OF EACH EPOXY SYSTEM

Component	Properties
B47	Light yellow liquid; specific gravity of 1.6
XR40	Pale yellow liquid; specific gravity of 1.2
RA100	Colorless; reactive; corrosive
K450	Yellow-orange liquid; crystallization point is around room temperature

4.2 Methodology

To evaluate the bonding effect between our formulation and low carbon steel, we carried out pull-out tests for the formulations attached to low carbon steel. The experiment was guided by ASTM D3164M-03, the "standard test method for strength properties of adhesively bonded plastic lap-shear sandwich joints in shear by tension loading" (ASTM, 2003).

4.2.1 Material

In this project, we selected low carbon steel to make the coupon required in ASTM D3164M-03. The reason for using low carbon steel is that the wells that we are aiming to abandon are offshore wells. In offshore wells, low carbon steel is the first option for most well casings and tubings. The low carbon steel sheet is 0.031 in. with tolerance of +/-0.0015 in. It has been cold-rolled when manufactured. The surface is smooth and not corroded at all.

The epoxy systems that we applied in the test are the same formulation with barite as mentioned above in Table 3.

4.2.2 Pretreatment

Our experiments were carried out in an ideal condition. Real-world applications are likely to be affected by corrosion and ocean organisms. We didn’t rough the surface of coupon by either mechanical or chemical methods. The real situation cannot be easily evaluated by just randomly roughing the surface. In terms of those wells that haven’t been in use for a long time, casing and tubing might be either severely corroded or covered by aquatic organisms, or both of them. It is hard to find any reference or criteria to rough the surface that could represent the real offshore casing surface. We decided to take the ideal test results as a reference.

4.2.3 Preparation of samples

We cut the low carbon steel sheet into small coupons following the dimensions in ASTM D3164-03. **Fig. 12** shows the schematic of our lap-shear sandwich joint. We modified the preparation according to the material that we could find.

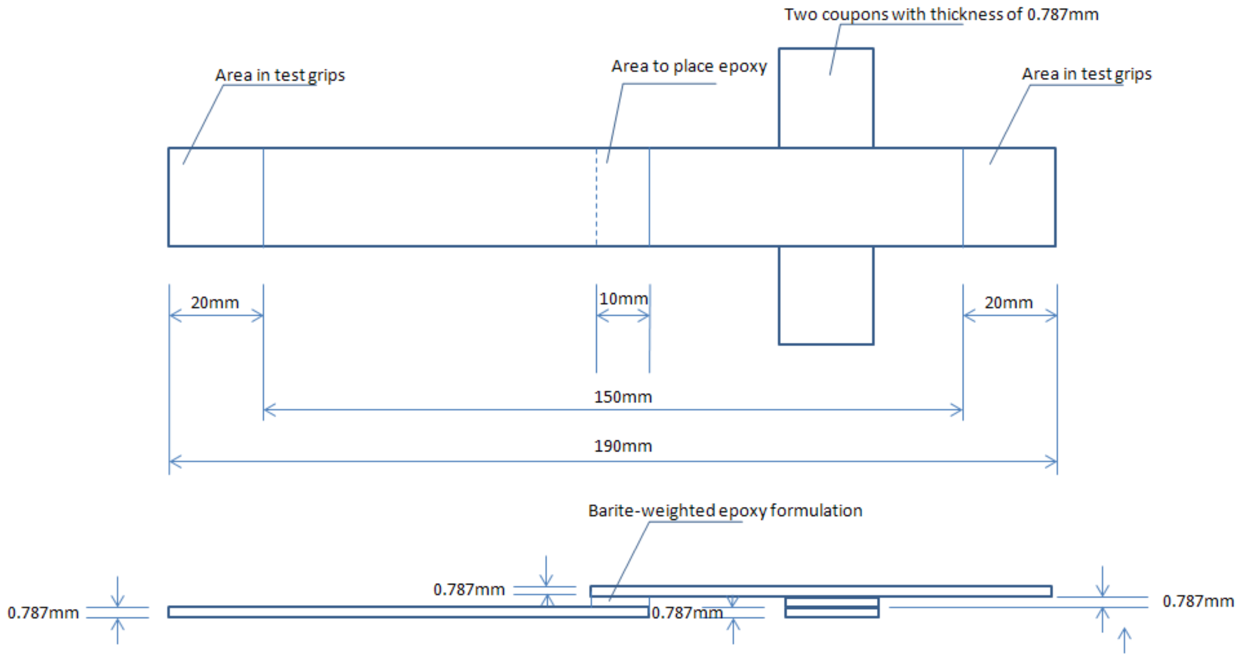


Fig. 12–**Schematic and dimension of lap-shear sandwich joint**

The main procedure of preparation is:

1. Make specimens that conform to the form and dimensions shown in Fig. 12.
2. Apply the barite-weighted epoxy in the designated area.
3. Place the specimens in the heating oven for certain amount of time before actually doing the shear test

Two coupons below the sandwich joints are used to support the upper coupon and to guarantee the epoxy formulation in between is 0.787 mm thick.

The most difficult part of the preparation is to spread the barite-weighted epoxy formulation on the surface of the coupon in the designated area. Ensuring repeatability of the test depends on exact placement of the epoxy on the coupons. The amount of the epoxy cannot be either too much or too little, which both lead to inaccurate test results. Also, the thickness of the epoxy insert will influence the joint strength obtained in this test due to the added offset. To eliminate the influence as much as possible, we were careful to repeat every step as identically as possible.

Moreover, to eliminate the influence of any nuisance variable, randomizing the order of all the runs in each experiment is extremely important. The experiment is generally a completely randomized single-factor experiment with six levels of the factor for each epoxy system. The levels of the factor are sometimes called treatments, and each treatment has eight observations or replicates. The levels are denoted as A to F, where the amount of barite increases from A to F. Each of these levels is repeated 8 times. Fig. 13 shows the order of preparation in one epoxy system. Experiments are run from A1 to F1, A2 to F2, and An to Fn where n is 8. This order helps to eliminates uncertainty.

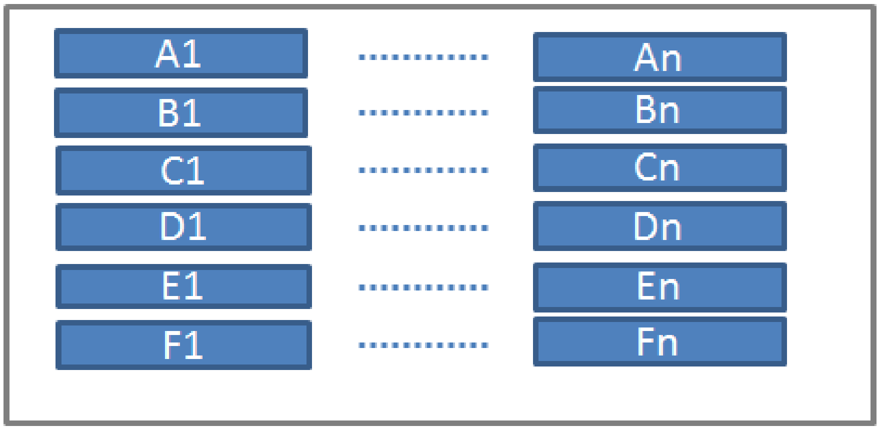


Fig. 13–Schematic of preparation

4.2.4 General information of mechanical tests

The procedures to hook up the equipment and test the specimens are listed as below:

1. Turn on the machine and preheat the heating facility in **Fig. 14** to the target temperature.
2. Take the specimens preheated in the oven in our lab and transport them as quickly as possible to the material test equipment.
3. Hold the specimens by two vertical grips, and set up the software.
4. Following the randomization principle, and do the pull-out test batch by batch.
5. Record the peak load that specimens are able to stand.

We used the MTS Insight^{TM} Electromechanical Testing System, consistent with ASTM D3164-03's requirement. When the heating facility reached the objective temperature, the designed tension load was added to pull the specimens vertically. The load added was set at 160 kgf/min.

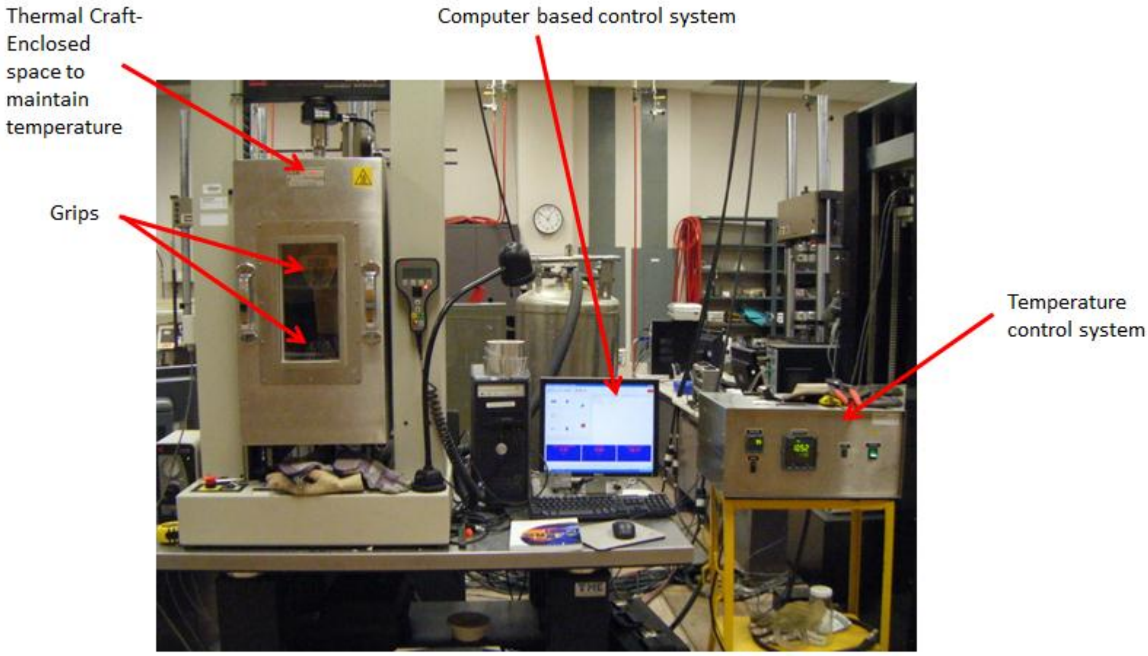


Fig. 14–The equipment for all the shear bond strength tests.

4.3 Filler loading influence on shear bond strength test

We added different amounts of barite into two potential epoxy formulations and generated two epoxy systems. We tested shear bond strength under 200°F, which is a reasonable average reservoir temperature in Gulf of Mexico (Haeberle, 2005) for 24 hours before carrying out the mechanical tests.

The procedures of the mechanical tests were following the general step listed in last chapter.

1. Make specimens that conform to the form and dimensions shown in Fig. 12. The order of making specimens followed Fig. 14.
2. Apply 12 different treatments of the barite-weighted epoxy in the designated area.
3. Place the specimens in the heating oven for 24 hours before actually doing the shear test.
4. Turn on the machine and preheat the heating facility in Fig. 14 to the target temperature 200°F.
5. Take the specimens preheated in the oven in our lab and transport them as quickly as possible to the material test equipment.
6. Hold the specimens by two vertical grips, and set up the software in the computer-based control system.
7. Follow the randomization principle, and do the pull-out test batch by batch.
8. Record the peak load that specimens are able to stand.

The **Table 5** below shows the components of each formulation/treatment.

Table 5–COMPONENTS OF EACH FORMULATION

	Barite added to the formulation, g					
Bisphenol A system	Aa	Ab	Ac	Ad	Ae	Af
	0	1.3	5.3	8.5	13.5	16
	Barite, wt%					
	0	17	46	57	68	72
	Barite added to the formulation, g					
Bisphenol F system	Fa	Fb	Fc	Fd	Fe	Ff
	0	1.3	5.3	8.5	13.5	16
	Barite, wt%					
	0	16	44	55	66	70

For each barite-weighted epoxy formulation, we made and tested eight identical specimens under same conditions. However, whether the specimens prepared are good or not cannot be evaluated until the pull tests are finished. The wettability, viscosity and density, all influence the thin film spread covering the designated area. The quality also might change after they were placed into the heating oven. This is mainly because of viscosity change when being heated. The epoxy formulations were not able to stand in between the two coupons when it became less viscous. To eliminate the variables' influence, we recorded all the data from the tests and eliminated the ones that didn't visually look fabricated well (Seen the samples on the right of **Fig. 15**). When extrapolating the data, we did the average for the rest of values. Fig. 15 shows how the elimination work was done. The samples on the left are those meeting the requirements of ASTM D3164-03, while the ones on the right are failure samples than cannot be accounted into our data extrapolation.

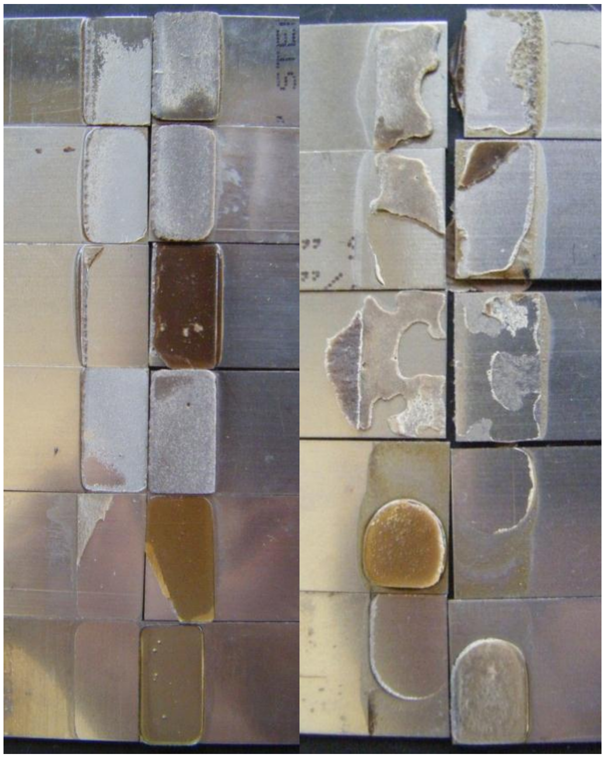


Fig. 15–Screening qualified samples for the test. The samples on the left are those well fabricated, with which we extrapolated the data. The samples on the right are the examples being eliminated.

According to the data recorded by the computer system (Seen in appendix Table A), we generated the trends in **Fig. 16**. For bisphenol A system, shear bond strength was deteriorated as barite weight percentage increases up to 72 wt%. According to the data that we had in our research, it has a minimum bond strength value, which comes at around 68 wt%. Compared to the bisphenol A system, the bisphenol F system data shows better stability in the data collected in Fig. 16. Also it shows that shear bond strength was very slightly increased by filler weight percentage increasing up to 70 wt%. The figure below also tells us that bisphenol A system is more filler sensitive compared to that of bisphenol F system.

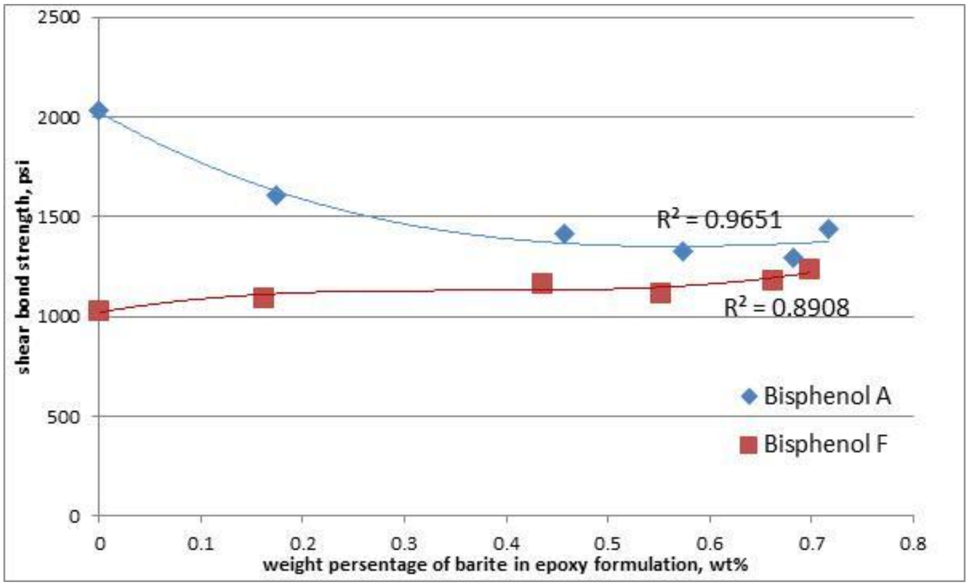


Fig. 16–Bond strength of bisphenol A system was deteriorated as fillers increase. Bond strength of bisphenol F system stays stable as fillers increase.

4.4 Simulated environmental tests

Our simulated environmental tests showed that when epoxy contacts steel in the presence of synthetic seawater, the epoxy/steel bond strength is decreased.

In our simulated environmental tests, we placed both systems in synthetic seawater for one hour before spreading it on the coupon, and then heated the specimens for 24 hours before the shear bond strength tests. We chose to test three treatments for each epoxy system. 6 observations were recorded by each treatment. For all the barite-weighted epoxy formulations, we did the same elimination as the previous tests, and extrapolated the data by doing an average for each formulation.

The procedures of the specific experiment are listed below:

1. Prepare the mixture with barite. Three different treatments for each epoxy system. So there are overall six treatments.
2. Prepare the synthetic seawater according to the geophysical and geochemical signatures research of the Gulf of Mexico (Joye et al., 2005). The synthetic seawater components are listed in **Table 6**.
3. Dump half of the mixture into the vials which contain the synthetic seawater and soak them for one hour as shown in **Fig. 17**. The vials were shaken some to increase the contact with the synthetic seawater, which is also shown in Fig. 17.
4. Dispose of the synthetic seawater, take the mixture out of the vial and spread it on the designated area on the coupon, which is shown in **Fig. 18**. Make specimens that conform to the form and dimensions shown in Fig. 12. The order of making specimens followed Fig. 14.
5. Place the specimens in the heating oven for 24 hours before actually doing the shear test.
6. Turn on the machine and preheat the heating facility in Fig. 14 to the target temperature 200°F.
7. Take the specimens preheated in the oven in our lab and transport them as quickly as possible to the material test equipment.
8. Hold the specimens by two vertical grips, and set up the software in the computer-based control system.

9. Follow the randomization principle, and do the pull-out test batch by batch.
10. Record the peak load that specimens are able to stand.

Table 6–SYNTHETIC SEAWATER FORMULA

Component	Amount, g/l
$MgCl_2 \cdot 6H_2O$	2.2
$CaCl_2 \cdot 2H_2O$	1.6
KCl	3.2
Na_2SO_4	4.1
$NaCl$	23.6

The density of the synthetic seawater is 8.31 ppg.

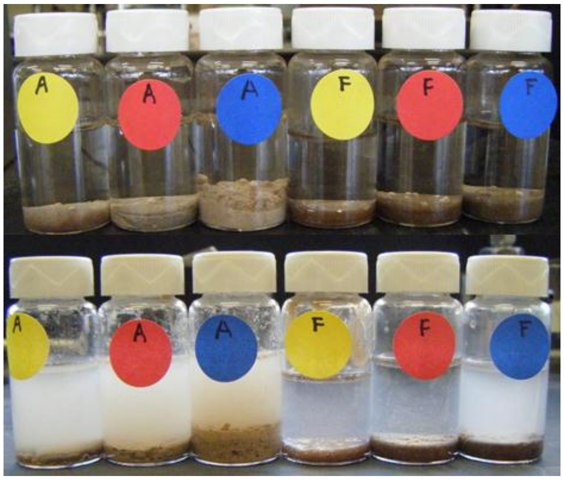


Fig. 17–We soaked and shaked the samples in synthetic seawater for one hour before pull-out tests. The upper one is shown what samples look like before shaking. The lower one tells barite in A epoxy system is easier to come out after shaking.

Fig. 18–After one hours of being soaked in synthetic seawater, the epoxy was mixed with synthetic seawater. The left three samples are for A epoxy system. The right three are F epoxy system's samples

The results show the significant decrease of bond strength when introducing the synthetic seawater into the formulation. The data obtained from our shear bond strength test are presented in Table 7 and **Fig. 19**. The solid bars in Fig. 19 represent the original test results without being soaked in the synthetic seawater. The no-fill bars show the results with treatment in the synthetic seawater. All the bond strength was reduced significantly by introduction of the synthetic seawater. Most of reduced data are less than the North Sea criteria—725 psi, except one treatment of BPA with 17 wt% barite. The 725 psi-criteria is given by the Netherland. The UK Offshore Operation Association has the similar criteria, which is given as 500 psi (dash line in Fig.19). If we use the UK's criteria, most of the treatment after simulated environmental test can meet the requirement. The original result listed in appendix Table B shows that the data of BPA looks quite erratic, while data of BPF are consistently stable. It also verifies our conclusion in previous test that the BPA is more barite sensitive than BPF system.

Table 7–SIMULATED ENVIRONMENTAL TEST DATA AT 200℉

Name of system	Barite, wt%	Soaked	Average bond strength, psi
BPA	72	N	1527
BPA	72	Y	560
Difference			967
BPF	70	N	1163
BPF	70	Y	322
Difference			841
BPA	57	N	1320
BPA	57	Y	551
Difference			769
BPF	55	N	1126
BPF	55	Y	615
Difference			511
BPA	17	N	1544
BPA	17	Y	875
Difference			669
BPF	16	N	1113
BPF	16	Y	565
Difference			548

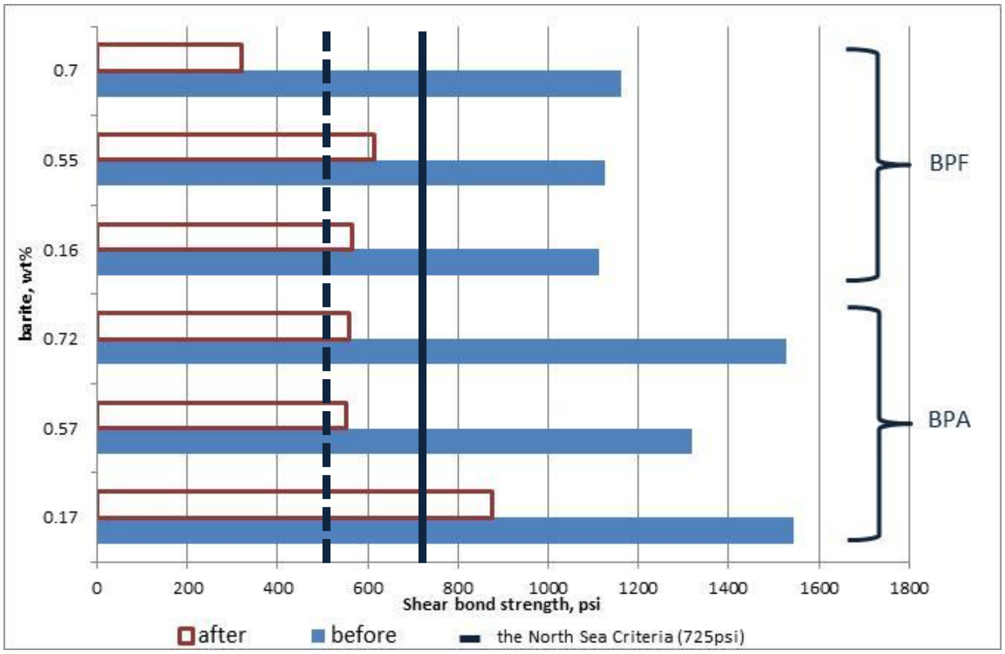


Fig. 19–Two formulations with different weight percentage of barite show the same results. Shear bond strength decrease with the introduction of the synthetic seawater into the epoxy system

In order to analyze the reasons why this phenomenon happens, we looked into the observations during the simulated environmental test. The **Fig. 20** shows the difference between samples with and without being soaked in the synthetic seawater. The upper one is a sample mixed with the synthetic seawater, while the bottom one is pure formulation with the same amount of barite which was not experienced simulated environmental treatment. The upper one shows the uneven surface and different reflection which is caused by the introduction of the synthetic seawater. The light colored part in Fig. 18 shows what the barite looks contacting with the synthetic water. The light colored areas of BPA system are definitely larger than that in BPF system. The barite separation of BPA is more obvious than that in BPF in Fig. 17. So larger light colored areas are most likely attributed to that more synthetic seawater was introduced into the system, which leads to the greater reduced-bond-strength/original-bond-strength ratio (ROR). The ROR values can be calculated by the equation below. The **Fig.** 21 and the **Fig. 22** show the comparison of what samples look like after pull-out test with or without being placed in the synthetic seawater. From the pictures of both BPA and BPF systems, the introduction of the synthetic seawater into the formulation, leads to not only loose texture, but also the reduction in contact area of epoxy and low carbon steel. This can be applied to illustrate the deterioration of bond strength when the synthetic seawater was introduced into the system.

$$\text{ROR} = \frac{\text{original bond strength} - \text{bond strength in stimulated test}}{\text{orignial bond strength}}$$

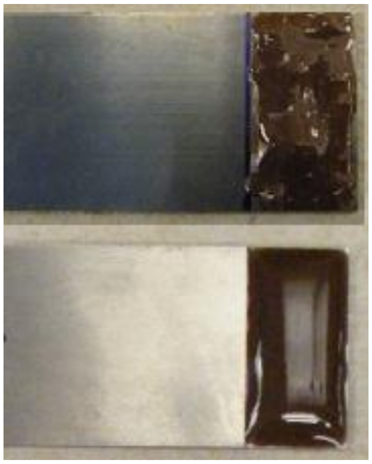
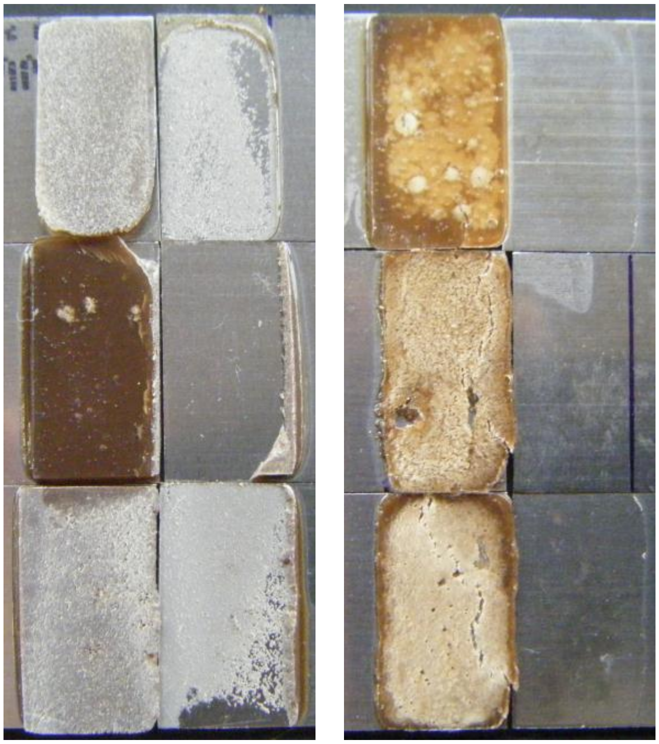


Fig. 20–Formulations mixed with/without the synthetic seawater were placed on the coupons.



BPA without being soaked by the synthetic seawater

BPA with being soaked by the synthetic seawater

Fig. 21– After shear bond strength at 200 °F, for BPA system, the texture on the right look looser and the contact area seems less than the ones on the left.

BPF without being soaked in the synthetic seawater

BPF with being soaked in the synthetic seawater

Fig. 22– After shear bond strength at 200 °F, for BPF system, the texture on the right look looser and the contact area seems less than the ones on the left.

Comparing all the six treatments, we put the reduced-bond-strength/original-bond-strength ratio (ROR) into **Fig. 23** to show the difference. And it is generated to evaluate the influence of the synthetic seawater in bond strength. The smaller the ratio is the better quality that the material has. The Fig. 23 shows the ratio varies between two systems. The ROR of BPA system increases as the barite is increasingly added, while ROR of BPA has a minimum value which comes at around 50 wt% barite. Based on the ROR, we would like to have the formulations with low ROR value, which is circled in Fig. 23. For BPA, low barite weight is recommended. For BPF, around 50 wt% of barite is recommended. While if economic factor is taken into consideration, the more barite we will use, the less expensive it will cost. So the BPF should be more economic at this point. Moreover, at most of barite weight percentage, ROR of BPF is smaller than that of BPA. It verifies our previous conclusion that BPA system is more seawater sensitive compared to BPF system one more time. However, if combined with the North Sea criteria, the BPF recipe still need some improvements to strengthen the bond strength.

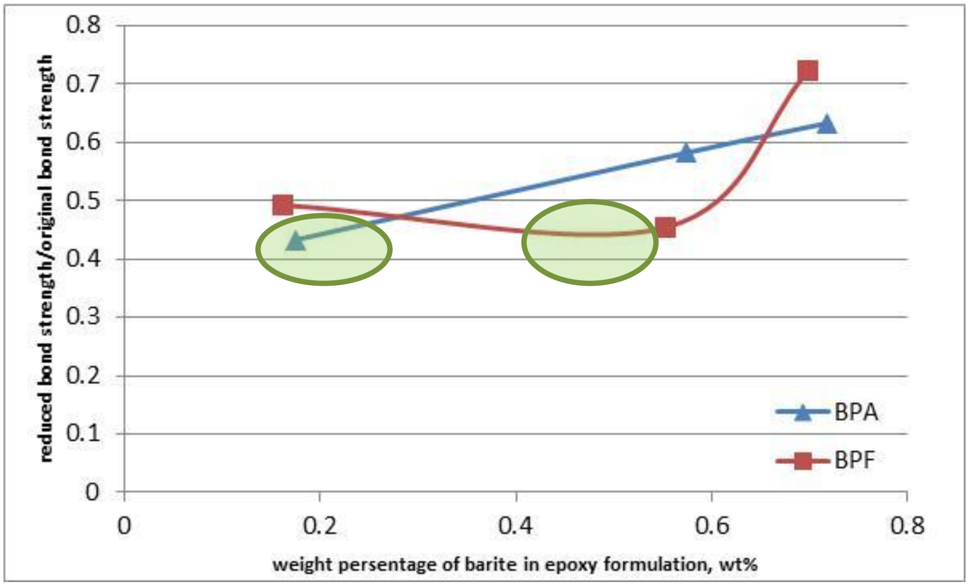


Fig. 23–Reduced-bond-strength/ original-bond-strength ratio varies between two systems at 200 °F-shear-bond-strength test.

Let’s assume we’ll set a plugging at a casing 1 ft long with inside diameter of 5 inches applying BPF formulation. We did calculation to see what the North Sea criteria-725 psi means to us quantitatively.

The surface area of inside tubing is

$$A_{in} = \pi Dh = 3.14 \times 5\text{in} \times 12\text{in} = 188\ in^2$$

The pounds of force A_{in} can withstand

$$F_{in} = A_{in}P = 188.4 in^2 \times 725 psi = 137000\ pound$$

The cross-section area of the tubing is

$$A_{cs} = \pi \frac{D^2}{4} = 3.14 \times \frac{5in \times 5in}{4} = 19.6\ in^2$$

The pounds of force exerted on the end of the plug

$$F_{cs} = A_{cs}P = 19.6\ in^2 \times 725 psi = 14200\ pound$$

Comparing the F_{in} and F_{cs}, if the bond strength of BPF/barite system bonded to steel is 725 psi, then a one-foot length in the wellbore will hold nearly ten times the force of a delta p of 725 psi in a five inch casing. So even if the strength is even further degraded, there is very large margin for error.

To conclude the simulated environmental tests, mixing with synthetic seawater did deteriorate the bond strength between barite-weighted epoxy and low carbon steel. However, the influence varies among different treatments. The more barite sensitive, the more reduction in bond strength it will cause. BPF performs more stable, economic in retaining bond strength after simulated environmental treatment.

4.5 Bond strength development tests

We did bond strength tests to see what influence the time will have on the bisphenol F system. The results show that epoxy/steel shear bond strength continues developing over the next 6 days, even though the resin hardening time (curing time) is far shorter than that.

In our previous research, we determined the relationship of the epoxy formulation with different weight percentage of barite and curing time (hardening time). Our laboratory work shows curing time is not equal to the time that the formulation needs to develop complete bond strength.

We prepared all the specimens same as that shown in Fig. 12 and carried out the pull-out tests by the same equipment in Fig. 14, and then did average calculation to analyze the data. All the original lab data can be found in appendix C.

Compared to the 2 hours curing time we obtained for the formulation with 66 wt% of barite, the bond strength keep developing for the next 6 days (see in **Fig. 24**). To reach the maximum based on our one-week test, the forecast in Fig. 24 shows it might need more than 6 days. Also, from the Fig. 24, it shows the bond strength can reach 725 psi of the North Sea Criteria around 10 hours, which is far shorter than 24 hours of cement hardening time (Kenneth et al. 2010).

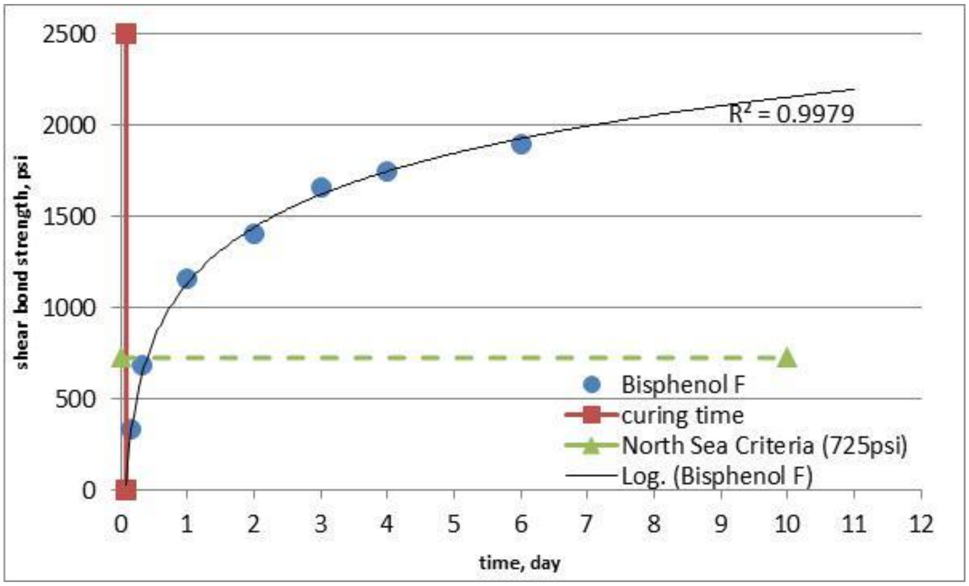


Fig. 24–The bond strength continues developing even after hardening time at 200 °F.

4.6 High temperature tests

We also carried out high temperature test to see the performance of epoxy material in high temperature, in case there are some wells located in high temperature formation. 200°F is a reasonable average reservoir temperature in Gulf of Mexico (Haeberle, 2005). The BPF does give us really excellent bond strength at 200°F. However, when increased the experiment temperature, the shear bond strength decreased significantly.

We did the high temperature test followed the procedure below:

1. Mix the F epoxy formulation with 13.5g barite.
2. Prepare all the samples in room temperature
3. Fabricate all the samples in heating oven either at 250°F or 300°F

4. Preheat the material test system shown in Fig. 14 at target temperature and transport the samples as quickly as possible to the material test equipment.
5. Hold the specimens by two vertical grips, and set up the software.
6. Following the randomization principle, do the pull-out test one by one.
7. Record the peak load that specimens are able to stand.

The results can be found in appendix D. The average values are shown in **Fig. 25.** The bond strength peak load at 250°F reduced 66% of bond strength compared to the one at 200°F. And the peak load at 300°F is only 18% of the bond strength at 200°F. The bond strength degradation is consistent with literature published by Benjamin J (2011). However, the reduction extent in other literature shows less than what we had in our experiment (Adamvalli and Parameswaran, 2008). There are some equipment limitations in our experiment that we cannot avoid. Take an example, we cannot not fabricate samples and pull out tests in the same heating facility. The interval to transport the samples might change the thermal history. The slight change in thermal history has influence on thermal expansion character. After a cooling down and heating up process, it is most likely to reduce the bond strength. Especially, when the fabricating temperature is high, the influence is much greater. The transportation interval for samples at 200°F experienced an around-100°F-temperature-drop process. While, for the one at 250°F experienced an around-150°F-temperature-drop process. And for the one at 300°F, it was a 200°F temperature-drop. The temperature factor at high temperature has greater influence on bond strength. So the higher temperature value might be underestimated in this way. Also, in Benjamin J's paper, they proved that high temperature could cause weight adhesion loss as a result of aging and degradation. Their tests were carried out at temperature at 220 ℃ and plus, which is even higher than the temperature requirement in our proposal. All in all, one thing is undoubted that the bond strength is turning weak when the temperature goes up.

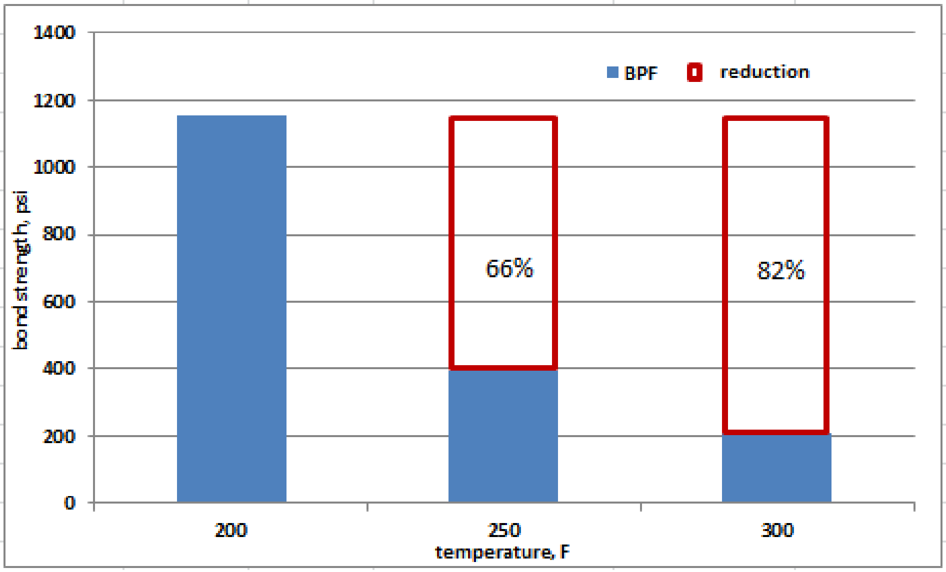


Fig. 25–Bond strength of F epoxy decreases as temperature goes up.

4.7 Discussion

As our research progressed, it became clear that the bisphenol A system had some undesirable characteristics that we would not like to see. Besides BPA's bond strength sensitivity to barite, which has been discussed in previous portions, the flow-ability at higher barite loadings was worse for BPA.

When they were shaken for the simulated environmental test, we could see the ability of flow-ability for the bisphenol A system is worse than that of the bisphenol F system, especially when barite addition is increased. When gathering all the simulated pictures together in Fig. 26, we can easily figure out that the difference of flow-ability in the bottom vials is obvious. It's more difficult for BPA with 71 wt% barite to flow as BPF did. The formulations in the vials with yellow and red sticker are hard to tell the flow-ability difference.

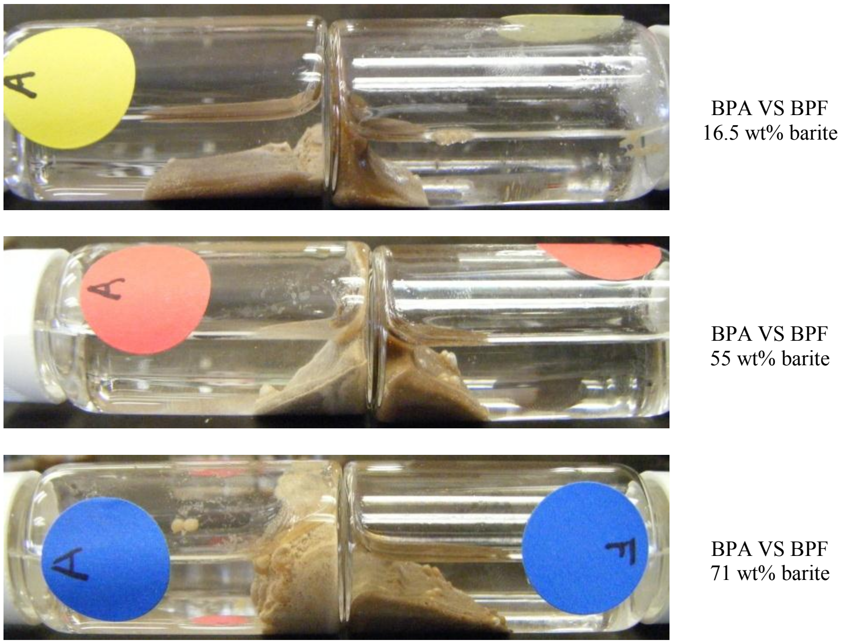


Fig. 26–The picture of flow-ability comparison among different treatments.

According to regulation established by The Netherland sector in Dutch mining authority guidelines, a plug on the borehole had to be tested with pressure min 725 psi inflow test (Liversidge et al., 2006). In our research, our laboratory results give us average bond strength of the bisphenol F formulation from 1010 psi to 1160 psi as barite increased from 0 up to 70 wt% barites. The average bond strength of the bisphenol A formulation has minimum value of 1290 psi with 68 wt% barite, and maximum value of 2140 psi which appears at 0 gram of barite added. Both epoxy system meet the requirement. However, the BPF system is stable at bond strength both with and without the synthetic seawater treatment, while BPA system is much filler sensitive than BPF system. Also, in the simulated bond strength tests, formulations of BPF didn't meet the North Sea criteria. So improvement in the formulation might be needed in the future.

4.8 Limitations

Our tests were carried out in an ideal condition. In the real world, applications are likely to be affected by corrosion and organisms along the wall. In our tests, we didn't do any pretreatment on the surface of low carbon steel, either mechanically or chemically. Tubings and casings in the real world are not as smooth as what we had in our tests. Corrosion and organisms along the casing can increase the contact area which contributes to increase fictions and bond strength as well. At this point, corrosion and organisms might be something that we could take advantages of. Epoxy might not be the only material that we are going to apply in abandoned offshore wells in the GOM. Bentonite is also being considered. With bentonite, or any other heavier materials placed on the top of epoxy formulation, it would help epoxy to withstand more pressure differential than the value obtained in our pull-out tests.

Also, if we combine moisture and high temperature influence onto this barite-weighted epoxy system, the bond strength might be weaken more severely. One paper showed the temperature increasing might activate the process of absorbing moisture into the reinforced epoxy system, which leads to adhesion loss and bond strength reduction (B.C, 2006). Their experiments were actually tested in room temperature. We are also limited by our laboratory equipment and cannot carry out this complex effect experiment either. However, based on our previous work, we can have a general prediction that combining both moisture and high temperature weakens the bond strength. The extent need to be evaluated.

CHAPTER V

CONCLUSIONS

Previous research in our lab has shown resin hardening time increased with the amount of barite added, which is good to give sufficient time to complete the abandonment work. Tests in this project were carried out in ideal conditions. Real world applications are likely to be affected by corrosion etc. Shear bond strength tests in this study showed further properties of epoxy systems:

1. A large number of mechanical tests verified that the shear bond strength of bisphenol F type epoxy bonded to low carbon steel remained stable when barite filler was added to the formulation.
2. Simulated environmental tests demonstrated that when epoxy contacts steel in the presence of synthetic seawater, shear bond strength decreases. We suspect that the strength decrease is due to the epoxy-steel contact area being decreased and the bond thus weakened due to some capture of some seawater between epoxy, steel, and epoxy, barite.
3. Even though strength reduction must be accounted for in determining pressure differential that the epoxy-steel bond can withstand, bisphenol F system with barite bonded to low carbon steel retains sufficient shear bond strength to exceed all established regulations.
4. Epoxy-Steel shear bond strength continues developing for six days, much longer than hardening time and reaches 725 psi more rapidly than cement formulations.

5. Increasing temperature weakens the bond strength of the barite-weighted epoxy with the low carbon steel. At least a portion of the observed weakening is due to unavoidable temperature cycling caused by the necessity of curing the samples in a separate oven from the testing device oven.
6. Even with weakening at high temperature, the shear bond strength of BPF/barite system bonded to low carbon steel is strong enough so that even a short length of plug in a wellbore will meet the most stringent regulatory criteria.
7. The BPF/barite system should be evaluated in a test wellbore where the epoxy system must drop through several thousand feet of synthetic seawater and bond to a section of steel casing in order to demonstrate strength of the bond under more realistic conditions.

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APPENDIX A

Table A–Shear bond strength of different treatments, kgf/cm^2

Barite,g	Observations of BPA								Average, kgf/cm2
	1	2	3	4	5	6	7	8	
0		133.74	327.03	315.17	312.10	362.93	333.02	215.9	142.85
2.8	259.81	362.90	283.33	218.89	133.63		129.59	190.41	112.75
5.3	262.57	226.38	151.28	252.46	151.28	252.46	134.00	157.04	99.58
8.5	239.99	186.94	193.22	221.80		140.64	136.80		93.28
13.5	158.59	144.61	221.96		124.96	194.44	238.59	188.21	90.81
16	284.56	112.84	135.64	267.51	157.76	188.65	180.31	288.77	101.00
	Observations of BPF								
0	172.22	207.61	145.31	128.21	125.95	121.54	142.53	109.31	72.04
2.8	195.61	147.95	111.86	205.66	168.99	152.10	136.13	113.16	76.97
5.3	191.05	173.73	141.98		111.071		186.90	179.79	82.04
8.5	157.53	176.16	183.33	122.26	125.40	155.82	176.95	158.37	78.39
13.5	162.38	153.63	159.03	187.29	151.56	145.49	206.86	162.68	83.03
16	129.54	163.96	188.13	185.29	183.32	165.07	191.39	184.67	86.96

Table B–Shear bond strength data from simulated environmental tests, kgf/cm^2

Name of system	Barite, wt%	1	2	3	4	5	6	Average bond strength, kg/cm2
BPA	72	101.22	85.49	76.56	84.08	87.57	37.75	78.78
BPA	57	38.212	35.19	40.06	68.03	170.58	112.89	77.49
BPA	17	93.73	120.81	90.73	94.32	162.44	176.59	123.10
BPF	70	40.80	44.92	51.70	38.19	44.18	51.78	1278.99
BPF	55	90.22	93.84	77.25	96.92	81.12	79.54	300.21
BPF	16	62.81	67.21	63.49	78.94	98.26	106.17	978.78

Table C—Shear bond strength after different fabrication time, $\mathrm{kgf/cm^2}$

Time, hr	1	2	3	4	Average, kg/cm2
2 hr	0	0	0	0	0
4hr	52.04	58.56	37.39	41.825	47.45
8hr	92.67	86.38	107.25	97.82	96.03
48hr	265.89	142.33	179.50	200.57	197.07
72hr	219.45	263.30	217.00	140.58	210.08
96hr	278.71	248.08	243.94	215.01	246.43
144hr	230.24	270.89	280.11	282.68	265.98

Table D–Shear bond strength at high temperature, $\mathrm{kgf/cm^2}$

Temperature, F	1	2	3	4	5	6	7	8	Average, kg/cm2
200	162.38	153.63	159.03	187.29	151.56	145.49	206.86	162.68	162.68
250	43.27	54.72	55.84	50.62	54.46	59.88	61.54	55.517	392.37
300	28.63	25.58	28.76	29.61	32.95	30.06	28.65		207.23

VITA

Name: Zhuo Gao

C/O Dr. Robert Lane

Address: Department of Petroleum Engineering

Texas A&M University

3116 TAMU - 501 Richardson Building

College Station, TX, 77843-3116

Education: B.S., Oil&Gas Storage and Transportation Engineering,

China University of Petroleum (East China). 2008

M.S., Petroleum Engineering, Texas A&M University. 2011

Email Address: peggysayhi@gmail.com