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Safety and Technical Considerations in Well-Stimulating Ships and Proposed Key Rule Requirements

PART- I

Safety and Technical Considerations in Well-Stimulating Ships

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Abstract: **Carrying and handling acids on board well stimulating ships provokes challenges for regulators and operators, due to its links with hazards, risks, and safety concerns.**

This paper seeks to offer a clear overview of safety and technical aspects in well stimulating ships in Part I of the paper and highlights a set of key rule requirements as guidance to stakeholders involved in the applications of these types of ships, in Part II of the paper. The measures implied in proposed rule requirements to eliminate, prevent, contain, mitigate, and control any potential hazards and their consequences of carrying acids in well stimulating ships are explored in Part II of the Paper.

The core contents indicate the extent to which a ship's design, installation and operation are prepared for well stimulating ships in new ship construction, retrofits, and ship in service.

Keywords: **Well Stimulating Ships- Well Stimulation-Matrix Acidizing-Fracturing-Safety of Ships-Risk Assessment/Analysis of Ships-Safety Design-Safety Barriers(layers)-Classification Society Rules-Offshore Support Vessels- Chemical Tanker- Dangerous Goods.**

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1. INTRODUCTION

Well stimulation methods, historical background, details about the main two basics categories of well acid treatments: Matrix Acidizing and Fracture Acidizing are introduced.

Well stimulation ships' features include main particulars of typical Hydrochloric acid tanks, typical arrangement, construction details, equipment and systems are given and explained.

The world's marine well stimulation ship fleet analysis is addressed.

The main properties and hazards of acid treating fluids commonly used in well stimulating ships are compiled by the author and presented in simplified Tables.

The utmost goal and outcome of this technical paper was stressed as to participate in highlighting a consolidated and comprehensive provisional rule requirements intended for the Construction and Classification of Offshore Well Stimulation Ships.

The starting points and the foundations of this study are the perceived hazards and risks of handling acids and to amend the old LR provisional rules for well stimulation ships with additional modifications, consolidations, and enhancements.

In this study, various existing classification society rules, standards, codes, regulations, and references which are relevant to well stimulation ships were consulted, explored, and utilized. The experience of the author from involvement in well stimulation ship retrofit projects and previous employment with other classification societies is utilized as well. The proposed applicable rule requirements are given.

In well stimulating ships, the carriage and use of acids introduce challenges for regulators and operators. In fact, due to the different chemical/physical characteristics of acids, its link with the safety, hazards, and risks arising from using acids are explored and discussed.

The paper indicates and analyzes the key safety and technical considerations interrelated and triggered by the potential hazards and risk-related items associated with carrying and handling acids on board well stimulating vessels. It explored in detail the measures implied in applicable rule requirements to eliminate, prevent, contain, mitigate, and control the relevant potential hazards and their consequences.

Emphasizing the proactive approach, and considering tackling the potential hazards, and risks associated with acid properties and the necessary counter measures as well as the controls required in the design, installation, and operational safety barriers (layers) were identified, explored, and analyzed by the author.

This paper provides a clear overview, simple and essential set of guidance to stakeholders involved in the applications of well stimulating ships. It will be helpful for regulators, ship owners, designers, shipyards, ship operators and researchers, plan approval engineers and field surveyors and indicate the extent to which a ship's design, installation and operation are prepared for well stimulating ships in new ship construction, retrofits, and ship in service.

2. WELL STIMULATION

Is a well intervention performed on an oil or gas well to increase or restore and improve the flow and production of hydrocarbons from the drainage area into the well bore.

Stimulation process is the opening of new channels in the rock for oil and gas to flow through easily and by well stimulating, the hydrocarbon bearing foundation is improved near the well bore.

Sometimes, a well initially exhibits low permeability, and stimulation is employed to commence production from the reservoir. Other times, stimulation is used to further encourage permeability and flow from an already existing well that has become under-productive.

2.1 Methods of well stimulation [1] [2] [3]

Well stimulation is generally accomplished through three primary well stimulation processes: acidizing (acid injection) or sometimes called Solvent Stimulation, fracturing(hydraulic), and sometimes even the use of explosives. However, some references prefer to classify the stimulation processes under two types of acid treatment: matrix acidizing or simply acidizing and fracture acidizing or simply fracturing.

Other methods are used but in a limited scale such as steam injection and waterflood injection and CO2 Injection.

2.1.1 Steam Injection

Steam is one type of stimulation technique for increasing production in zones of high-viscosity oil by injecting steam into the formation to improve the oil's flow properties. High-temperature equipment and appropriate workover procedures and relevant rules are required when steam injection is used to stimulate production.

2.1.2 Waterflood Injection and CO2 Injection

Waterflood injection and CO2 injection is not so common.

It is a method used to increase production from an existing reservoir by injecting water into the reservoir to displace the oil.

Such method is suitable for reservoirs that are geologically bounded on at least three sides since the water is trapped in place and considered a nearby source.

CO2 injection (or “CO2 flood”) is a process by which carbon dioxide gas is injected into the reservoir to replenish drive energy and recover additional oil instead of being left in the reservoir. CO2 is often present in certain gas reservoirs in conjunction with hydrocarbon gas. Gas processing plants separate the CO2 from the hydrocarbon gas and send it to pipelines for transport to the field for injection.

While other types of simulation treatments also used such as “Steam Injection” and “Waterflood Injection and CO2 Injection,” acidizing and fracturing remain the most common types of well simulation used today.

2.2 ACIDIZING-Historical Background

The first oil well acidizing treatments where the use of acids to stimulate or to improve oil production from carbonate reservoirs was first attempted in **1895**. Patents covering the use of both hydrochloric and sulfuric acids for this purpose were issued at that time.

Although several “well treatments” were conducted, the process failed to arouse general interest because of severe corrosion of well casing and other metallic equipment.

Attempts to use acid occurred **between 1925 and 1930**, which consisted of using hydrochloric acid (HCI) to dissolve scale in wells in the Glenpool field of Oklahoma and to increase production from the Jefferson limestone (Devonian) in Kentucky. None of these efforts were successful and “acidizing” once again was abandoned. [1]

It was not until the selection of effective acid systems and discovery of efficient corrosion inhibitors during the 1930’s that significant success was achieved, and then the practice became popular. This delay of nearly 40 years pointed out the importance of selecting the right fluid products for well stimulation. [2]

The discovery of arsenic inhibitors which allowed HCI to react with the formation rock without seriously damaging the metal well equipment, revived interest in oil well acidizing in **1932.**

Ever since, many changes and innovations have been made to improve the effectiveness of acidizing treatments over the years. These continue to improve the effectiveness of the acid treatments for the stimulation of production and injection wells in both sandstone and carbonate formations. Studies of the acid, reservoir and oil chemistry and physics have evolved significantly, but the basic concept of acidizing is still that of dissolving rock or flow obstructions from the reservoir to the well and improving the flow of fluids to and from the wellbore.

Well stimulation acidizing has become a highly skilled science. A knowledge widened and accumulated about the available materials, acid formulations, additives, techniques, technology used, chemical reactions at treating and well conditions, reservoir properties, rock characteristics, merits, and hazards and how to eliminate or mitigate them and the interrelationship of the several factors involved to design and optimize an effective and efficient acidizing treatment.

Below are further details about the main two basics categories of well acid treatments: Matrix Acidizing and Fracture Acidizing:

2.2.1 Matrix Acidizing

Acidizing is a process done by injecting acid solution into the well and into the pores of the reservoir rocks, which dissolves either reservoir rock or damaging materials blocking the pore spaces of the rock. Those may include a portion of the rock and deposits including mud solids, limestone, dolomite, and calcite cement between the sediment grains of the reservoir rocks, which restricts the production tubing perforations.

Acidizing will lead to enlarging the natural pores, increase effective permeability of the reservoir, stimulating the flow pattern of oil and eventually increase well production.

Originally, acidizing was applied to carbonate formations to dissolve the rock itself. Over a period, special acid formulations were developed for application use in sandstone formations to remove damaging materials induced by drilling or completion fluids or by production practices.

Matrix acidizing may be selected as a proper technique for one or more of the following reasons:

a. To remove either natural or induced formation damage.

b. To achieve low-pressure breakdown of the formation before fracturing.

c. To achieve uniform breakdown of all perforations.

d. To leave zone barriers intact.

e. To reduce treating costs.

2.2.2 Fracture Acidizing (Hydraulic Fracturing)

Fracturing techniques were developed in 1948 and the first commercial fracturing treatments were conducted in 1949. [1]

While in Matrix Acidizing, the acid flow is confined to the formation's natural pores and flow channels at bottom-hole pressure below the the formation hydraulic fracturing pressure (low pressure enough to keep from fracturing the reservoir rock), but in Acid Fracturing the injection of acid through natural or induced formation fractures occurs above hydraulic fracturing pressure.

This type of stimulation enlarges or creates flow from the formation to the wellbore.

The primary purpose of fracturing is to achieve injectivity or productivity beyond the natural reservoir capability. **Fracturing** involves injection of oil or water-based fluids at highly pressurized acid into the well and rock foundation, leading to fracturing the reservoir rock, inducing cracks and dissolving the inhibitive sediments and create a new permeability path, interconnect existing permeability streaks, and promote channels through which the hydrocarbons can flow through the rocks.

Fracture ("frac") fluids include oil, water, acid, emulsions, foams, or combinations of these. The frac fluids are pumped downhole under high pressure at a high rate of flow to fracture the formation.

An acid fracture job (often called "acid frac") involves pumping a gelled acid at a pressure above the formation fracture limit. The gel creates a fracture, and the acid etches the rock surfaces, creating an irregular pattern.

2.2.2.1 Fracturing Techniques and Equipment

Fracturing treatments usually are performed by pumping materials down the casing or tubing at rates as high as well limitations and economics will permit.

Fracturing Equipment: Hydraulic Fracturing equipment consists of pumps and blenders, high-pressure manifolds and treating line, remotely controlled master valves, and tree savers. Pumping equipment is the conventional triplex pump, quintaplex pump, or a pressure-multiplier type of pump. However, in both types of acidizing, the effective stimulation process depends mainly upon creating and enhancing new extensive permeability channels to serve in transferring oil from the low permeability rock to the well bore.

Well stimulation may be done using a well stimulator structure or using offshore ships known as "Well stimulation Ships or Vessels".

3. WELL STIMULATION SHIPS (WSS)

A well stimulation ship is usually a special type of OSV (Offshore Support Ships) with its specialized arrangement, equipment, and installations. So, its special features can support in performing a variety of stimulation operations on the oil/gas wells located offshore. It is a ship specialized to provide occasional services for production of wells, inject stimulation substances into wells through the operation of well stimulation installations and equipment to improve the productivity of oil and/or gas and support the offshore engineering production.

The services performed by a well stimulation vessel may include:[2]

a. Handling and storage of well stimulation substances for transportation.

b. transporting well stimulation substances and well fluids between onshore and offshore facilities. **c**. Performing well stimulation operation on site of the oil/gas wells at sea.

The scope of this paper is applied to marine systems and does not cover industrial systems for well stimulation operation except safety systems.

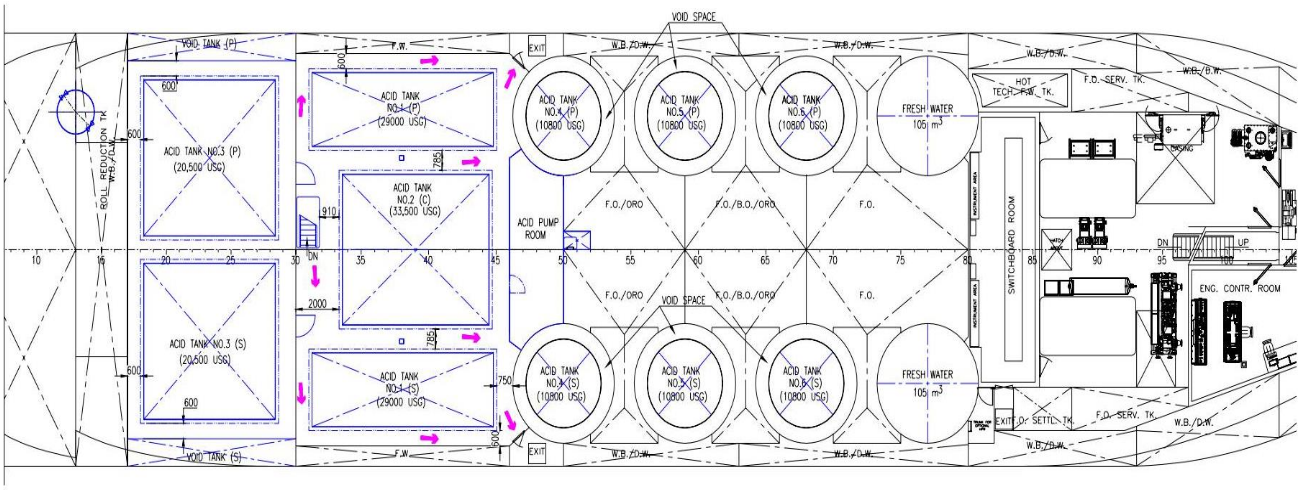
In the following sections, the well stimulation ships arrangement and construction features, and the world's marine well stimulation ship fleet analysis are explored.

3.1 Well Stimulation Ship Arrangement and Construction Features

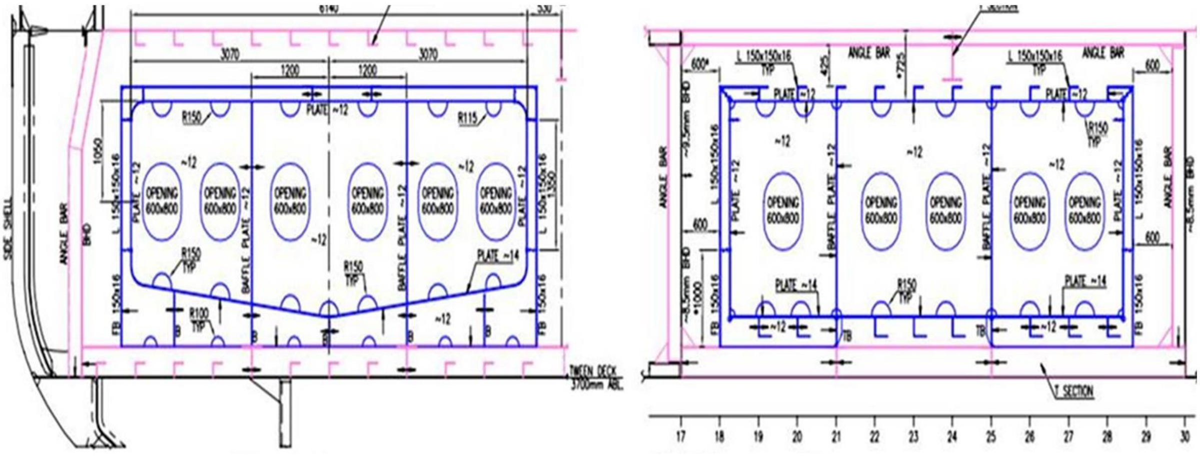
Table (1) was compiled to indicate the main particulars of typical HCl acid tanks on board well stimulation ships.

Table (1) Main Particulars of Typical HCl Acid Tanks on board of Well Stimulation Vessels	
Cargo	HCl acids with a concentration of **32%** HCl with a density of **1.20** MT/m3
Design pressure	**30 psi & 40 psi** (P/V relief valve positive setting pressure). [3]
Tank geometric shape	Prismatic & vertical cylindrical.
Tank Dimensions/ volume	▪ **For prismatic tank:** Length:8.40xBreadth:2.90xHeight:4.78 and 6.80mx5.90mx3.35m and 6.10mx6.14mx2.25m ▪ **For Vertical Cylindrical Tank:** diameter of 3.50m x height of 5.225m. [3]
Tank structure and arrangement	External stiffening. Details as per given Figures.
Tank material	▪ **For prismatic tanks:** LR Grade EH50 (plates and stringers) & LR Grade EH36(stiffeners). ▪ **For cylindrical tanks:** LR Grade EH36. [3]
Corrosion allowance	2.5mm
Tank coating/lining	DERAKANE 411-45 coating, suitable for **32 %** HCL @ **50** Deg C.
Applied Rules & Regulations	▪ LR Chemical Tankers Rules & LR Rules and Regulations for Classification of Sips, Part 5, Chapter 10 & Ch.11 (Steam Raising Plant and Associated Pressure Vessels/Other Pressure Vessels). ▪ Hull structural requirements of OSV Chemical Code - Code for the Transport and Handling of Hazardous and Noxious Liquid Substances in Bulk on Offshore Support Vessel ▪ IMO Resolution A.1122(30) – Code for the Transport and Handling of Hazardous and Noxious Liquid Substances in Bulk on Offshore Support Vessels (OSV Chemical Code).
Structural Analysis used tools	The structural modelling of tanks and supporting structure has been carried out using the software FEMAP (v11.3.3) and the analysis is performed using NASTRAN solver.

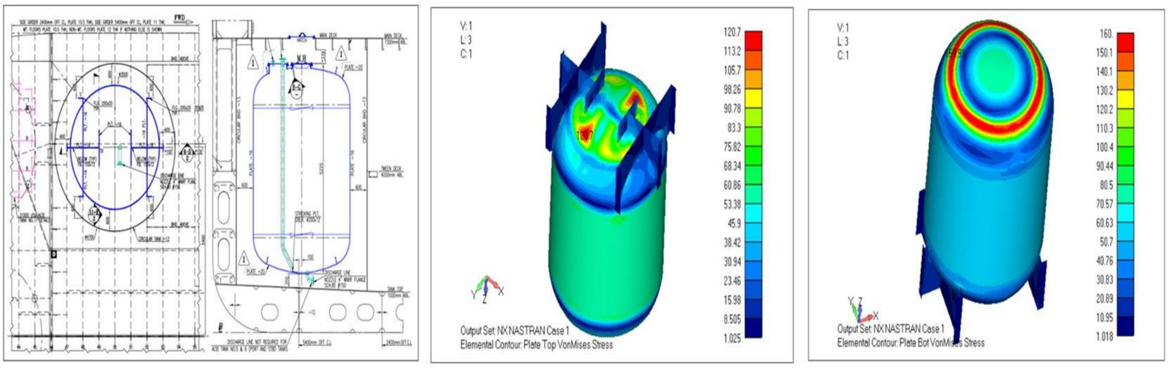
Figure (1) shows typical arrangement and construction details of well stimulation HCl acid tanks located under deck and Figure (2) shows HCl acid tanks (prismatic and cylindrical types) during fabrication phase. [3]



Key General Arrangement Plan



Typical Acid Tanks Construction Details and Arrangement (Prismatic type & located below deck)



Plan in way of HCl Acid Tank(Cylindrical Type)

Plate Top Von- Mises Stress (MPa) -Allowable 181.48 MPa

Plate Bottom Von- Mises Stress (MPa) -Allowable 181.48 MPa

Strength Analysis of HCl Acid Tank & Foundation Structure

Figure (1) Typical arrangement and construction details of Well Stimulation HCl Acid Tanks located under deck [Curtesy of OML (Overseas Marine Logistics L.L.C.)]

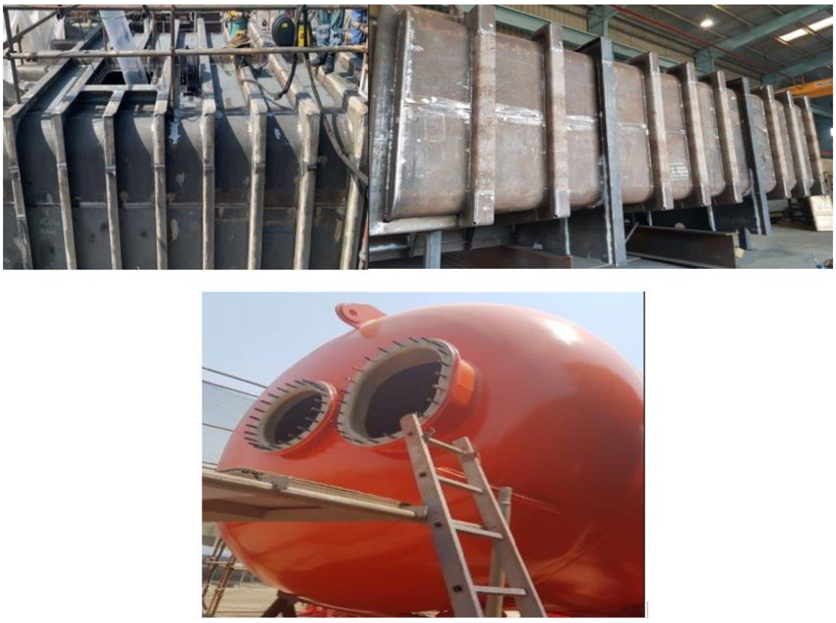


Figure (2) HCl Acid Tanks (prismatic and cylindrical types) during Fabrication Phase [Curtesy of OML (Overseas Marine Logistics L.L.C.)]

3.2 Well Stimulation Systems and Equipment

As detailed earlier, **stimulation systems** are the facilities installed on vessels for the purpose of stimulation of wells to improve their productivity of oil and/or gas.

Unless requested by the owner, equipment and systems used solely for well stimulation operations are in general not subject to classification by LR, provided they are designed and constructed in compliance with an applicable recognized standard. However, the following rule requirement is recommended:

•***The recognized standards used in design of well stimulation equipment are to be specified by designer and acceptable to LR. A manufacturer's, confirmation statement, affidavit, or other acceptable documentation to verify compliance with applicable recognized standards is to be submitted to LR.***

Their installations and onboard testing are to be supervised in the aspects of operational safety as to reduce to a minimum any potential hazards, risks, or danger to safety of personnel, vessel structures and equipment on board and marine pollution.

Well stimulation equipment installed on the offshore service vessel is consisting of, but not limited to, tanks, pumps, compressors, piping systems and related subsystems and components such as: control screens and instruments for acid handling in control room, mixers and blenders for uninhibited acid and other chemical additives, liquid additive skids, chemical pumps, acid pumps, high-pressure injection pumps, filters, hoses and hose reels, injection manifolds, and hydraulic power units (HPUs). Well stimulation ships are sometimes also equipped with a dynamic positioning system.

The equipment shall be designed and built according to recognized regulations and safety standards.

Well Stimulation Equipment and Systems may include surface equipment and subsea equipment:
a. **Surface equipment** may include acidizing equipment, fracturing blenders, pumping units, hydration, and chemical additive systems, supporting equipment such as coiled tubing, lifting equipment, well control equipment, pressure vessels, piping and electrical components, control systems, etc.

b. **Subsea system** and equipment may include well control package, lubricator, etc.

Figure (3) illustrates Photos of typical HCl acid processing equipment located above deck on board a ship classed by Lloyd's Register. [3]

Figure (3) Photos of Typical HCl Acid Processing Equipment on board a ship classed by Lloyd's Register [Curtesy of OML (Overseas Marine Logistics L.L.C.)]

3.3 The world's marine Well Stimulation Ship Fleet Analysis [4] [5] [6] [7] [8]

Analysis of survey information reveals that **the world's marine Well Stimulation Ship fleet** increased in number and shifted geographically in early-2000s. Up to the year 2022, the world fleet increased 25% to a total of about **33 ships**. DMC: they have **33** registered.

The market continues to change, with several notable additions and subtractions to the global stimulation ship fleet. As major key players in oil and gas industry, **Halliburton** maintains the world's largest number of well stimulation ships with about 10 vessels in its fleet. **Schlumberger** retains the industry's second-largest fleet with about eight stim vessels. **BHGE** has the world's third-largest fleet of stimulation ships with about seven ships in its fleet. **AL MANSOURI** has now five stim ships.

The distribution of the WSS fleet was concentrated in the Gulf of Mexico, an area that contains almost 60% of the total world fleet. The remainder of the fleet remained deployed in South America, North Sea, the Middle East, and West Africa. West Africa, South America, and the Canadian North Atlantic regions were listed as the areas of best future growth potential.

The trend towards larger ships continued. The average vessel length increased to 70.41 m (231 ft). About 41% of the vessels were greater than this average. Cruising speeds still average about 12 knots and the average engine horsepower increased to 3,780 hp. It goes without saying that the statistics mentioned are only indicative at the time of writing this paper and subject to change with the time.

There are noticeable differences in the storage/tankage location philosophies and preferences among vendors. Acid, additive, and gas storage capabilities, above and below deck, dominate this difference. Wide variation in above-deck storage capabilities is evident. The trend is moving towards more total storage capability.

The increased demand by national and international governing- bodies for better environmental performance encouraged continued development of more environmentally friendly fracturing fluids. Average fracture-pump hydraulic horsepower increased 8%, to 8,500 hhp, with some vessels having greater than 10,000 hhp. The average number of pumps per ship remained between five and six, with five vessels having eight or greater.

Improvements in measurement and monitoring systems dominated retrofit upgrades and new-build vessels in this type of ship market. So far most of the focus on WSS has been from a new construction viewpoint. Recent construction trends continued to lean toward new design/ constructions over retrofitted existing ships. There are opportunities arising for retrofitting conversions as reported recently in middle east for AL MANSOURI and ADNOC, where the authors were heavily involved.

4. ACIDS AND ACID TREATING SOLUTIONS (SOLVENTS): MAIN PROPERTIES, FEATURES, AND HAZARDS

Acid formulations may be applied in either matrix or fracture-type treatment, depending on the degree of stimulation or production increase sought.

There are primary requirements that an acid must meet to be acceptable as a treating fluid as follows:

a. It must react with carbonates or other minerals to form soluble products.

b. It must be capable of being inhibited to prevent excessive reaction with metal goods in the well.

c. Other important considerations are safety handling, availability, and reasonable economical costs.

Recognizing the main properties of acids used in well stimulation ships is significantly helping to identify the potential hazards and risks in storing and handling acids on board. It is the crucial starting point to establish and consolidate the relevant safety and rules and regulation requirements.

Various kinds of acids and additives are available, so that treating fluids can be tailored to meet individual well needs.

Acids, acid treating solutions, its main properties, features, and hazards are discussed in the following sections.

4.1 Acids commonly used in Well Stimulating Ships

Despite the dozens of formulations available, only four major types of acid are suitable for well stimulation and have found extensive application in well treatments: (1) Hydrochloric acid, (2) hydrofluoric acid, (3) acetic acid, and (4) formic acid. [1]

Hydrochloric acid is the most eminent type of acid in this application. It is used both to remove rust, scale, or limestones and dolomites, from the rock, and undesirable carbonate deposits in oil wells to encourage the flow of crude oil or gas to the well which is called "stimulation." [9]

Also, HCI can be combined with mud acid, or hydrofluoric acid (HF), and used to dissolve quartz, sand, and clay from the reservoir rocks.

HCl and other acids which are used for acidization are of **hazardous nature either to personnel or to equipment.** Due to the corrosivity of these acids, it can cause harmful burns. Acid fumes are irritating for eyes and respiratory system. Their vapors are irritating to the skin and mucous membranes and in concentrated solutions it can cause severe flesh burns. Accordingly, proper handling with caution and efficient design and operations in this concern will be of the utmost importance.

Hydrochloric acid is **extremely corrosive** to metals including the following: carbon steel, stainless steel, nickel, Monel, bronze, brass, copper, Inconel, and aluminum. Great care should be taken to avoid contact with these materials with hydrochloric acid.

Figure (4) shows a hole due to HCl leakage from rubber coating because of severe corrosion in way of the suction nozzle of an acid tank.

Figure (4) a hole resulting from severe corrosion due to HCl leakage from rubber coating in way of the suction nozzle of an acid tank [The photo was taken during the author experience with GL]

Hydrochloric Acid is also **highly corrosive** to the skin and mucous membranes and can cause severe burns to any part of the body especially the eyes which exposure to it or its vapors immediately cause severe irritation.

Direct contact with hydrochloric acid may cause partial or total visual impairment or blindness can occur.

Hydrochloric acid has **excellent warning properties to human senses.** Concentrations of 0.3 parts per million (ppm) can be detected by smell, and concentrations above five parts per million will cause discomfort. [9]

Many organic acids are available, but the four most used are: **Acetic Acid, Acetic Anhydride, Citric Acid, and Formic Acid.**

The most common two organic acids, **formic and acetic,** are used less frequently in acidizing. They are suited primarily for wells with high temperatures or for conditions where prolonged reaction times are desired.

Hydrofluoric acid (HF): HF is used primarily to remove clay particle damage in sandstone formations and is used primarily for sandstone acidizing.

HF acid attacks silica and silicates, such as glass and concrete. It will also attack skin, natural rubber, leather, certain metals such as cast iron and many organic materials.

Hydrofluoric acid is poisonous, alone or in mixtures with hydrochloric acid, and should be handled with extreme caution.

4.2 Acidizing Additives

Acidizing additives are chemicals added to acidizing treatment mixtures to modify their properties in order to adapt these fluids to tailor them for the particular well, formation and reservoir fluid conditions. The use of additives, and their relative concentrations are dependent on the formation, fluid, and well properties.

4.2.1 Corrosion inhibitors

the use of a corrosion inhibitor as an additive made possible the first commercially feasible acidizing treatments. Since that time, many auxiliary chemicals have been developed to modify acid solutions, influencing their application and recovery.

Typically, all treatments require a corrosion inhibitor, and an iron sequestrant, as the acid will always react with the metals in the surface equipment and tubulars.

Inhibitors are chemical materials that, when dissolved in acid solutions greatly retard the reaction rate of the acid with metals which are used in acidizing to avoid damage to casing, tubing, pumps, valves, and other well metallic equipment.

It is important to note that inhibitors cannot completely stop all reaction between the acid and metal: however, they do slow the reaction, eliminating 95 to 98% of the metal loss that would otherwise occur. [1]

Most inhibitors have practically no effect on the reaction rate of acid with limestone, dolomite, or acid-soluble scale deposits.

Moreover, in order to protect the integrity of the already completed well, **inhibitor additives** are also introduced to the well to prohibit the acid from breaking down the steel casing in the well.

After an acid job is performed, the used acid and sediments removed from the reservoir are washed out of the well in a process called **backflush**.

4.3 Liquefied gases

Liquid nitrogen and liquid CO2 are sometimes used in acid solutions to provide added energy for better well clean-up. Nitrogen also is used to make formed acid, which provides excellent leak off control in low permeability rock. [1]

Specific requirements for cryogenic liquid nitrogen tanks, drip protection, venting and vent outlets from Nitrogen tanks, and ventilation of spaces for liquid nitrogen shall be met. Those will be addressed in the relevant sections of this paper.

Tables (2), (3), (4) & (5) give the main properties and hazards of acid treating fluids (sometimes called solutions or solvents) commonly used in well stimulating ships as compiled by the author from several references. [1][2][9][10][11][12]

Full details of the properties and health and safety implications of WS acids can be found in their relevant Material Safety Data Sheet (MSDS) as well.

Table (2) Hydrochloric acid (HCl): Properties, use, applications, advantages, and disadvantages	
Physical Properties	Pure hydrochloric acid **(Muriatic**)is **a colorless liquid,** but it takes on a yellowish hue when contaminated by iron, chlorine, or organic substances.
	▪ It has **excellent warning properties.** Concentrations of 0.3 parts per million (ppm) can be detected by smell. ▪ HCl acid gas is easily dissolved in water. ▪ HCl acid gas that is a little heavier than air. ▪ Surface tension can be controlled to aid in: penetration, wetting properties, and reducing friction pressure.
Chemical Properties	Type of Acid: Mineral (an inorganic acid).
	Reactive Power: Strong.
	▪ Ordinarily supplied in concentrations of 32-36%. ▪ In well treatments, its normal strength has been 15% by weight.
Chemical Properties Application/ Use	Manufactured in concentrations of 32 to 36 wt. % HCl. Diluted for field use to 15, 20 or 28 wt. %.
	▪ 15 wt. % HCl has been the most used. ▪ Concentrations of 20 and 28% have become extremely popular over the past two decades.
	When pumped into a limestone formation, a chemical reaction takes place producing calcium chloride, CO2, and water as represented by the following equation: $2HCI+CaCO3 \longrightarrow CaCL2+H2O+CO2$
Chemical Properties /Advantages	Is the most widely used acid treating solution in well stimulation vessels because: ▪ It is the most efficient chemical available for improving the permeability of the formation and, ▪ It leaves no insoluble reaction product (or insoluble precipitates).
	It has an excellent reaction rate on limestone and dolomite formations.
	Easily inhibited to prevent attack on oil-field tubulars up to 204°C (400°F).
	Can be emulsified for slower reaction rate.
	Exhibit de-emulsification properties for rapid clean up.
	Most reaction products are water soluble and easily removed.
	Additives to minimize or eliminate insoluble reaction products can be applied.
Advantages	Available and used in far larger quantities than any other acid in the petroleum industry.
	It is the most economical and relatively low in cost
	Relatively easy to handle.
Disadvantages	▪ **It is however, not without limitations.** Hydrochloric acid is quite reactive; therefore, it will spend quite rapidly on some formations. ▪ It is essential with hydrochloric acid to size acid treatments and pump rates to optimize this property.
	HCl acid is of **hazardous nature either to personnel or to equipment:** ▪ Due of corrosively of these acids, it can cause harmful burns. ▪ Acid fumes are an irritant for eyes and respiratory system. ▪ Their vapours are irritating to the skin and mucous membranes and in concentrated solutions it can cause severe flesh bums. ▪ Hydrochloric acid is **extremely corrosive** to metals including the following: carbon steel, stainless steel, nickel, Monel, bronze, brass, copper, Inconel, and aluminium. ▪ Great care should be taken to avoid contact of these materials with hydrochloric acid. ▪ Hydrochloric Acid is a **highly corrosive** to the skin and mucous membranes and can cause severe burns to any part of the body especially the eyes which exposure to it or its vapours immediately causes severe irritation. ▪ Direct contact to hydrochloric acid may causes partial or total visual impairment or blindness can occur. ▪ Hydrochloric acid is listed in Section 112(b) of the Clean Air Act Amendments of 1990 as a Hazardous Air Pollutant (HAP). ▪ Concentrations above five parts per million will cause discomfort. ▪ Accordingly, proper handling with caution and efficient design and operations in this concern will be of the utmost importance.

Table (3) Acetic Acid (CH3COOH, or CH3CO2H, C2H4O2, or HC2H3O2): Properties, use applications, advantages, and disadvantages	
Physical Properties	▪ Is a colourless organic acid, Molar mass: **60.052 g/mol**, Density: **1.05 g/cm^3**, Boiling point: **118 °C**, Melting point: **16.6 °C.** ▪ It is called glacial acetic acid because, ice like crystals will form in it at temperatures of approximately **16° C (60° F)** and will solidify at approximately **9° C (48° F).**
Chemical Properties	Acid Type: Organic/ Retarded acids.
	Reactive Power: weak.
Chemical Properties Application/Use	Normal concentrations of **7.5% to 10%** when used alone.
	Mainly used in hydrochloric acid mixtures.
	Used as an iron control additive.
	Used in Carbonate acidizing.
	Perforating fluid.
	It is also recommended where acid must remain in contact with the well casing for many hours, as when acid is used as the displacing fluid on a well cementing job.
Chemical Properties/ Advantages	Is soluble in water in any proportion and in most organic solvents.
	Although mixtures of acetic acid with water (as used in well stimulation) are considered corrosive to most metal, the corrosion rate is far lower than that of hydrochloric and hydrofluoric acids.
	▪ Is easy to inhibit against corrosion. ▪ Is used frequently as a perforating fluid where prolonged contact times are required. ▪ Is sometimes used as a displacing fluid on a well cementing job, where the contact time may be hours or days before perforating takes place.
Advantages	Commercially available is approximately **99%** “pure”.
Disadvantages/ Hazards	▪ When used with aluminium, magnesium or chrome surfaces must be protected. ▪ Care should be exercised when handling acetic acid. ▪ Its solution in concentrated form can cause severe burns. ▪ Its fume inhalation can harm lung tissue.

Table (4) Formic Acid called methanolic acid (HCOOH or CH_2O_2): Properties, use applications, advantages, and disadvantages	
Physical Properties	▪ Is a low flammable, biodegradable, and stable liquid under ambient conditions. ▪ Boiling point of **101°C**, a freezing point of **8.3°C**. ▪ It is a colourless and clear. ▪ Corrosive liquid with a pungent odour.
Chemical Properties	▪ Acid Type: Organic/ Retarded acids. ▪ Reactive Power: weak. ▪ Is the simplest of the organic acids/ carboxylic acid and is completely miscible (capable of being mixed) with water. ▪ In solution it forms a stronger acid than acetic but weaker than hydrochloric acid. Otherwise, its properties parallel those of acetic acid. ▪ The concentration normally is limited to **8 to 10 %** because of the limited solubility of calcium format.
Application/Use	▪ Seldom used alone. ▪ Mainly used in hydrochloric acid mixtures. ▪ Is a corrosion inhibitor aid. ▪ Is most frequently used in combination with hydrochloric as retarded acid for high temperature (Hot Wells).
Advantages	▪ Hydrochloric acid solutions can be blended with formic acid to provide formulations having extended reaction times. ▪ Such mixtures are used to obtain more dissolving power per gallon of acid solution. ▪ Formic and acetic acids can also be blended.
Disadvantages/ Hazards	▪ Is vesicatory (having the power to cause blisters). ▪ It should be handled with care. ▪ Breathing in formic acid can cause irritation of eyes and nose, sore throat, cough, chest tightness, headache, and confusion. ▪ In severe cases it can cause breathlessness and wheezing. Skin contact with formic acid can cause pain, burns and ulcers. ▪ Formic Acid may damage the kidneys.

Table (5) Hydrofluoric acid (HF): Properties, use applications, advantages, and disadvantages

Physical Properties	▪ Hydrogen fluoride is a colourless, fuming liquid or gas with a strong, irritating odour. ▪ Hydrogen fluoride readily dissolves in water to form colourless hydrofluoric acid solutions; dilute solutions are visibly indistinguishable from water. ▪ Because its low boiling point of **19.38 ° C** (**66.9°** F), in the anhydrous form is often exceeded by the temperatures at which it is transported and pumped; it must be kept in special pressure containers when used in that form.
Application/Use	▪ Is used primarily to remove clay particle damage in sandstone formations. ▪ Occurs as a liquid either in the anhydrous form (where it is fuming and corrosive), or in an aqueous solution (as used in well stimulation). ▪ It is always pumped as an HCl: HF mixture. ▪ For Sandstone matrix acidizing. ▪ For removal of HCl insoluble fines.
Chemical Properties	▪ Acid Type: Mineral. ▪ Reactive Power: Strong. ▪ Highly corrosive capable of dissolving many substances and compounds like oxides.
Chemical Properties/ Application/Use	▪ Due to the formation of insoluble fluorides and complexes with calcium, the use in formations that contain over about **15%** carbonate is limited to using trace quantities of hydrofluoric acid (usually **0.25%**) in dolomitic formations, to speed up the reaction of HCl with dolomite. ▪ In well stimulation, HF acid is normally used in combination with hydrochloric acid. ▪ Mixtures of the two acids may be prepared by diluting mixtures of the concentrated acids with water or by adding fluoride salts to hydrochloric. ▪ The fluoride salts release HF acid when dissolved in HCl acid. ▪ Concentrations of HF in HCl solutions range from **0.5 %.** ▪ Normal concentrations **1.5% to 6.0%.** ▪ It reacts with silicate minerals. Therefore, is used primarily for sandstone acidizing.
Disadvantages/ Hazards	▪ HF acid attacks silica and silicates, such as glass and concrete. ▪ It will also attack skin, natural rubber, leather, certain metals such as cast iron and many organic materials. ▪ HF is poisonous, alone or in mixtures with hydrochloric acid. ▪ It should be handled with extreme caution.

5. SAFETY, RISKS, HAZARDS, AND TECHNICAL CONSIDERATIONS OF WSS CARRYING ACIDS

After a long painful journey of ship accidents, disasters, damages, spilled oil, spilled blood, and lost lives, it led to triggering most of the maritime conventions and influencing relevant classification society rules.

The Titanic disaster of 1912, in which 1,503 people lost their lives, led to the **SOLAS 74/78**. The Torrey Canyon ran aground in 1967 while entering the English Channel and spilled her entire cargo of 120,000 tons of crude oil into the sea. This led to **MARPOL 73/78** which was adopted in 1973 with different dates for entry into force for all six annexes, starting from 2 October 1983 (Annex I) to amendments of (Annex VI) 19 May 2005. Following the Erika tanker breaking into two in December 1999, causing severe oil pollution, IMO adopted a revised schedule for the **Phase-Out of Single-Hull Tankers**, which came into effect on 1 September 2003, with further amendments validated on 5 April 2005.The sinking of Herald of Free Enterprise in 1987 where 193 lives were lost, led to a mandatory **ISM Code** in 1998. Also, 9/11 terrorism attack led to ISPS Code adoption in December 2022 and final entry into force 01 July 2004. [13]

In 1993, the IMO MSC, the UK proposed a standard five step risk-based approach, which was termed **Formal Safety Assessment (FSA),** as a way of ensuring that action is taken before a disaster occurs where effective Proactive approach (i.e., anticipating hazards, rather than waiting for disasters) by using a systematic and structured process.

These conventions were not the end of the story since striving for continuous learning from other fields is inevitable.

The field of risk analysis in ships was utilized with connection of development of the ship design philosophy and starting to use different ways of thinking, the emergence of new terminologies and methodologies as well from “reactive” to “proactive approach”, from “prescriptive approach” to “risk-based approach”, goal-based approach and “Formal Safety Assessment”.

Bearing these concepts in mind, emphasizing the proactive approach, and considering tackling the potential hazards, and risks associated with acid properties and the necessary counter measures as well as the controls required in the design, installation, and operational safety barriers (layers) were identified, explored, and analyzed by the author.

Throughout the analysis implied the next sections, the author highlighted the safety and technical aspects and the specific applied rule requirements which are applied to well stimulation ships.

In well stimulating ships, the carriage and use of acids introduce challenges for regulators and operators. In fact, due to the different chemical/physical characteristics of acids, exposure to hazardous chemicals, hydrocarbon substances, low-flash point liquids, and handling cryogenic liquids in some cases, new risk scenarios need to be considered. For instance, encountering such hazards will mean some changes to the philosophy behind safety in terms of introducing new measures on board to counter their associated risks. Therefore, the acid plant storage, distribution systems and handling should not create a substantial risk resulting from the normal operation or any potential hazards of acid leakage or spillage".

The proactive approach is to be inherited in tackling the potential hazards and risks associated with acid properties, the necessary counter measures, and controls required in the ship design, installation and operational safety stages shall be addressed.

The concept in the design, construction, and operation of WSS is based on risk assessment. It should not be allowed if the consequences of an accident are unacceptable.

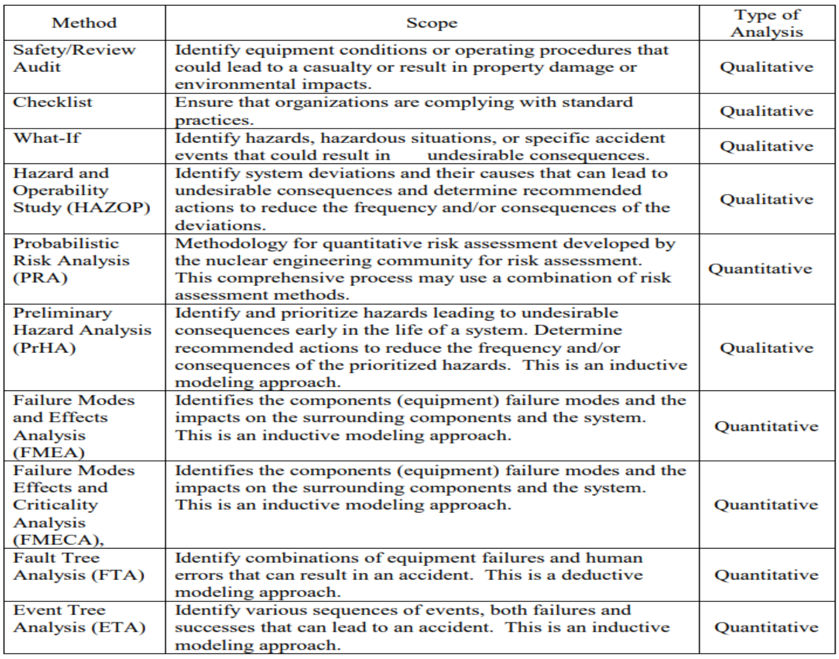
Risk assessment's prime objective is to ensure that 'risks arising from the use of acids affecting crew on board, the environment, the structural strength, or the overall integrity of the ship are to be addressed as a result of any damage scenarios.

Operational hazards and risks associated with physical arrangements need to be identified and eliminated wherever possible or mitigated (if a problem has occurred) as necessary.

Obviously, acid hazards and risks must be managed and controlled.

A risk analysis/Assessment: Process of evaluating the risk(s) arising from hazard(s), taking into account the adequacy of any existing controls, and deciding whether the risk(s) acceptable shall be performed for the ship pursuant to the recognized methods. The risk analysis shall be performed through the identification of undesired events, thoroughly understanding the hazards of acid use, an evaluation of the probability that they may arise and the associated consequences. The analysis shall be presented as early as possible during the planning and design phase. For any new or altered concept or configuration a risk analysis should be conducted in order to ensure that any risks arising from the use of acids are assessed. Hence, if any changes are made to the design, equipment, or procedures during construction or after the ship is placed in service, the risk analysis shall be updated. Table (6) lists the Quantitative and Qualitative Risk Assessment Methods. [24]

Table (6) Quantitative and Qualitative Risk Assessment Methods



Method	Scope	Type of Analysis
Safety/Review Audit	Identify equipment conditions or operating procedures that could lead to a casualty or result in property damage or environmental impacts.	Qualitative
Checklist	Ensure that organizations are complying with standard practices.	Qualitative
What-If	Identify hazards, hazardous situations, or specific accident events that could result in undesirable consequences.	Qualitative
Hazard and Operability Study (HAZOP)	Identify system deviations and their causes that can lead to undesirable consequences and determine recommended actions to reduce the frequency and/or consequences of the deviations.	Qualitative
Probabilistic Risk Analysis (PRA)	Methodology for quantitative risk assessment developed by the nuclear engineering community for risk assessment. This comprehensive process may use a combination of risk assessment methods.	Quantitative
Preliminary Hazard Analysis (PrHA)	Identify and prioritize hazards leading to undesirable consequences early in the life of a system. Determine recommended actions to reduce the frequency and/or consequences of the prioritized hazards. This is an inductive modeling approach.	Qualitative
Failure Modes and Effects Analysis (FMEA)	Identifies the components (equipment) failure modes and the impacts on the surrounding components and the system. This is an inductive modeling approach.	Quantitative
Failure Modes Effects and Criticality Analysis (FMECA),	Identifies the components (equipment) failure modes and the impacts on the surrounding components and the system. This is an inductive modeling approach.	Quantitative
Fault Tree Analysis (FTA)	Identify combinations of equipment failures and human errors that can result in an accident. This is a deductive modeling approach.	Quantitative
Event Tree Analysis (ETA)	Identify various sequences of events, both failures and successes that can lead to an accident. This is an inductive modeling approach.	Quantitative

In Part II of the paper a set of key rule requirements will be given as guidance to stakeholders involved in the applications of these types of ships. The measures implied in proposed rule requirements to eliminate, prevent, contain, mitigate, and control any potential hazards and their consequences of carrying acids in well stimulating ships are explored in detail in Part II of the Paper.

6. CONCLUSION

The work presented in this paper studied “Safety and Technical Considerations in Well Stimulating Ships and Proposed Rule Requirements”.

From the study, the following conclusions can be drawn:

1-A brief insight into well stimulation ship type features, hazards, and operation are explored and presented in simplified Tables and Figures.

2-The needed set of rule guidance was given as a basis for establishing solid guidelines and rules for well stimulation ships to provide support to stakeholders, field, new construction, conversion surveyors and plan approval engineers is explained emphasized.

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