



ISSN: 2588-5596

JGT

JOURNAL OF GAS TECHNOLOGY

Volume 7 • Issue 1 • Summer 2022 • www.jgt.irangi.org



Journal of Gas Technology, JGT

Volume 7, Issue 1, Summer 2022

Publisher

Iranian Gas Institute

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EISSN: 2588-5596

Open Access Journal

Journal of Gas Technology is a peer reviewed, open access journal.

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JOURNAL OF GAS TECHNOLOGY

Volume 7 / Issue 1 / Summer 2022 / Pages 4-13

Journal Homepage: <http://jgt.irangi.org>

Selection of Economically Optimum Operating Conditions in Complex Distillation Systems for NGL Fractionation Processes

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ARTICLE INFO

ORIGINAL RESEARCH ARTICLE

Article History:

Received: 5 March 2022

Revised: 24 April 2022

Accepted: 22 May 2022

Keywords:

NGL Fractionation

Operating Pressure

Multicomponent Distillation

Process Optimization

Heuristic

ABSTRACT

Implementation of innovative distillation systems in multicomponent distillation design is a complex task because of multitude design variables. Operating pressure is one of the most prominent and effective variables in the distillation columns, which affects capital and operating costs directly. Many heuristic and optimization based methods are presented to find optimal operating conditions of distillation columns. Since the natural gas liquids, NGL, fractionation process is a costly and an energy demand intensive process, the design and operation of these units may affect many important petrochemicals supply chain and whole natural gas processing plant. Herein a comparison has been made between an easy to use heuristic design method and a stochastic based optimization method with genetic algorithm to design the simple and complex multicomponent distillation columns sequences for NGL fractionation processes. The results demonstrate the heuristic method is faster but in complex distillation systems, is inaccurate. In the studied case of the NGL fractionation process, the calculated column pressure by a heuristic method showed up to 40% different in comparisons against stochastic optimization results. This error leads to a 3% increase of the total annual costs in the heuristic method, which may have a significant impact on the final design and change the evaluation distillation scenarios because of cumulative error effects.

DOR: [20.1001.1/JGT.2022.251683](https://doi.org/10.1001.1/JGT.2022.251683)**How to cite this article**A. Tamuzi, N. Kasiri, A. Khalili Garakani, Selection of Economically Optimum Operating Conditions in Complex Distillation Systems for NGL Fractionation Processes. Journal of Gas Technology. 2022; 7(1): 04 -13. (http://jgt.irangi.org/article_251683.html)

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Available online 22 September 2022

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1. Introduction

Separation processes are necessary in many (petro-) chemical processes and account for an estimated up to 70% of plant operations and capital costs (Nezhadfarid et al. 2018). Over the recent decades, because of the increasing energy costs and importance of greenhouse gas emissions reductions, improving the gas processing and petrochemical processes have been widely studied (Ivakkpour, Kasiri, 2009; Kiss, 2014). Increasing the process efficiency by using sustainable designs for conventional processes is a prominent solution for the global warming problem (Shahandeh et al. 2015). One of the energy demanding processes is the natural gas liquids (NGL) fractionation process. The natural gas obtained from field processing units after dehydration and treating, passes the NGL extraction unit and NGL enters the fractionation unit as under pressure feed stream (Manley 1998). The objective of this unit is fractionating the hydrocarbons with a train of distillation columns. The main products of this process are ethane, propane, butanes, and condensate which are separated by three distillation columns in a direct arrangement as the conventional design (Yoo et al. 2016). Innovative designs for this process are studied for using complex distillation columns, replacement by divided wall columns and effect of the operating variables in the design stage (Halvorsen et al. 2016; Long et al. 2013).

The high number of variables in the design of distillation columns such as pressure, reflux ratio, number of stages, feed and side streams stage locations and stream flow rates bearing about a complex design problem. In addition, the economic design and optimization of distillation systems are complicated because of dealing with non-convex cost functions and the trade-off between capital and operating costs (Lee et al. 2018). Pressure has a major influence on capital cost in terms of allowable stress of materials and wall thickness also on operating costs because of phase equilibrium and column temperatures, which affect utility costs and process configurations.

Since the low-temperature distillation is preferred, column pressures are determined by a desire to use the cold utility in the condenser as a heuristic rule (Luyben et al. 2016). Following this rule leads to the use of the inexpensive cold utility at the lowest possible pressure. On the other hand, the increase of the column pressure increases the bottom temperature and that may lead to high-pressure steam demand in reboilers. Higher column pressure equivalent to higher capital costs, interactions not considered in heuristic pressure determination methods. Accordingly, the optimization-based methods are developed to solve the current issue use stochastic optimization to minimize a desired objective function like total annual costs (Tahouni et al. 2010).

Many parameters might affect the NGL fractionation process operation in addition to column pressure. For example, the reflux ratio is one of the important distillation parameters that affect condenser and reboiler heat duty and column diameter as well as column height. The feed stage might change the temperature profile in the column and the side steam stage might affect product composition.

Finding the optimal operation conditions is very important in multicomponent distillation systems, especially in complex distillation configurations because of the reciprocal influence of operating variable, which brings about a complex problem. In the NGL fractionation processes, the desired pure products are separated in a multicomponent distillation system. The simple and complex competitive distillation sequences are presented for four-component distillations in which the simple sequences are used as simple distillation columns with one reboiler and condenser, one feed and two products and complex sequences are used as complex columns with more than one feed and side stream products (Khalili-Garakani et al. 2016 a).

Herein a comparison was made between the heuristic method and genetic algorithm (GA) optimization for simple and complex four-component distillation systems in order to

investigate the effects of operating pressure on the total annual costs in the NGL fractionation process. Also, the impact of the accuracy of the optimization method on complex distillation systems design parameters and operation and capital costs are scrutinized.

2. Methods

As mentioned, the pressure is the most influential variable on the operating condition of the distillation systems and should be determined in the first design stage. The utilized heuristic method for operating pressure selection

starts the analysis algorithm for the first column of the sequence and increases the operating pressure from atmospheric pressure to maximum allowable pressure (2861 kPa in this case) and calculate the condenser temperature to find the inexpensive cooling water or refrigerant based on the table 1a values. The procedure is repeated for other distillation columns of the sequence and the operating pressures are determined. The heuristic approach studies the operation conditions of the columns individually and does not consider the reciprocally influencing effects of columns on the sequence.

Table 1. Utility Specifications and Costs (Seider et al. 2017)

a) Cooling Utilities			
Utilities	Temperature (°C)	Price (\$/GJ)	
Cooling water	25	0.675	
Refrigerant1	-12	6.470	
Refrigerant2	-35	13.17	
Refrigerant3	-68	23.30	
b) Heating Utilities			
Utilities	Pressure (kPa)	Temperature (°C)	Price (\$/ton)
Low pressure steam	350	148	13.20
Medium pressure steam	1050	185	15.30
High pressure steam	3100	238	17.60

The optimization-based approach, analyzes all columns of the sequence simultaneously by the genetic algorithm. The optimization variables are the operating pressures of the columns and the objective function of minimization is the total annual cost (TAC) of the sequence. The TAC (\$/year) is calculated by Eq. 1 where C_{Cap} is the capital cost, C_{Op} is the operating cost, i is the interest rate (0.1) and n is the plant lifetime (10 years). The capital cost of a column is calculated by the summation of condenser cost (Eq. 2), reboiler cost (Eq. 3), vessel cost (Eq. 4) and tray costs for sieve trays (Eq. 5) where A (m²) is the heat exchange area, W (kg) is the vessel weight, D_i (m) is the column diameter and N_T is the number of trays [13]. The column diameters for

shortcut distillation columns are calculated by Eq. 6 where V is the vapor flow rate, RR is the reflux ratio, T_D is the distillate temperature and P is the column pressure (Cui et al. 2018).

The optimizer varies the shortcut columns operating pressures to calculate the reflux ratio, number of trays, feed and product locations, as well as reboiler and condenser heat duties by the Aspen plus. The results of the simulation are returned to the optimizer and TAC is calculated. GA operators generate the new individuals based on the results of these reciprocal calculations. But in Heuristic method the operating pressure of each column is increased lanyary and step by step and all above mentioned parameters are calculate for each pressure based on the

simulation results. These automatic data transformations and calculations between

MATLAB and Aspen Plus are done with Aspen and MATLAB linking methods (Appendix A).

$$TAC = C_{Cap} \times \frac{i(i+1)^n}{(i+1)^n - 1} + C_{Op} \quad (1)$$

$$C_{cond} = \exp \{11.4185 - 0.9228[\ln(10.76A)] + 0.09861[\ln(10.76A)]^2\} \quad (2)$$

$$C_{reb} = \exp \{12.3310 - 0.8709[\ln(10.76A)] + 0.09005[\ln(10.76A)]^2\} \quad (3)$$

$$C_V = \exp \{10.5449 - 0.4672[\ln(W)] + 0.05482[\ln(W)]^2\} \quad (4)$$

$$C_T = 468 \exp(0.486 \times D_i) \times N_T \quad (5)$$

$$D_c = \left[\left(\frac{4}{\pi V} \right) \times (D) \times (RR + 1) \times (22.4) \times \left(\frac{T_D}{273} \right) \times \left(\frac{1}{P} \right) \times \left(\frac{1}{3600} \right) \right]^{0.5} \quad (6)$$

Hyper-parameters of the GA such as population size and crossover fraction are optimized based on the order of issue and the optimization problem is solved multiple times to assure the results are globally optimum. The Winn-Underwood-Gilliland equations within the Aspen plus shortcut simulator are used to carry out the simulation of distillation sequence using Peng-Robinson equation of state. The simulation of the complex configurations is carried out by decomposing the complex distillation columns into simple thermodynamically equivalent units (Wang, Smith, 2005). The GA toolbox of the Matlab manipulates the simulator through Aspen-Matlab linking methods. The GA generates a population of operating pressures for all distillation columns and sends to Aspen plus simulator. The Aspen plus solves the simulation for fixed feed and products specifications and calculates the heat duties, temperature profiles, number of trays and reflux ratio for all columns. The simulation results are transferred to the Matlab where the GA calculates the TAC. These calculations continue until the GA is converged to the optimum TAC of a sequence.

The distillation column sequences for four-

component systems with three distillation columns are illustrated in Fig. 1. In these sequences, the feed stream is demonstrated by {F} and distillate, bottom, and side stream products are demonstrated by {I}, {II}, {S} respectively. The possible simple and complex distillation scenarios are generated by the separation matrix algorithm (Khalili-Garakani et al. 2016 b).

3. Casestudy

A significant portion of natural gas is NGL, which has a high economic value. The NGL fractionation process separates the ethane, propane, butanes, and condensate with the desired specification from natural gas liquids feedstock with three distillation columns. The feed and the products specifications of this process are shown in table 2. The feed stream pressure and temperature are 4238 (kPa) and 29.4 (°C) respectively. The main products are specified by A as ethane-rich product with 0.99% recovery of methane and ethane, B with 0.98% propane purity, C with 0.98% isobutene and normal butane purity and D as condensate with 0.99% pentanes recovery. The feed and products specifications are kept the same in all distillation scenarios.

Table 2. Feed and Product Specifications of NGL Fractionation Process (Yoo et al. 2016)

Components	Feed (kmol/hr)	A (molfrac)	B (molfrac)	C (molfrac)	D (molfrac)
Methane	61.9	0.02			
Ethane	2901.1	0.97	0.01		
Propane	1980.3	0.01	0.98	0.01	
i-Butane	461.4		0.01	0.31	
n-Butane	984.4			0.67	0.01
i-Pentane	286.4			0.01	0.36
n-Pentane	202.5				0.26
n-Hexane	203.9				0.26
n-Heptane	90.9				0.11

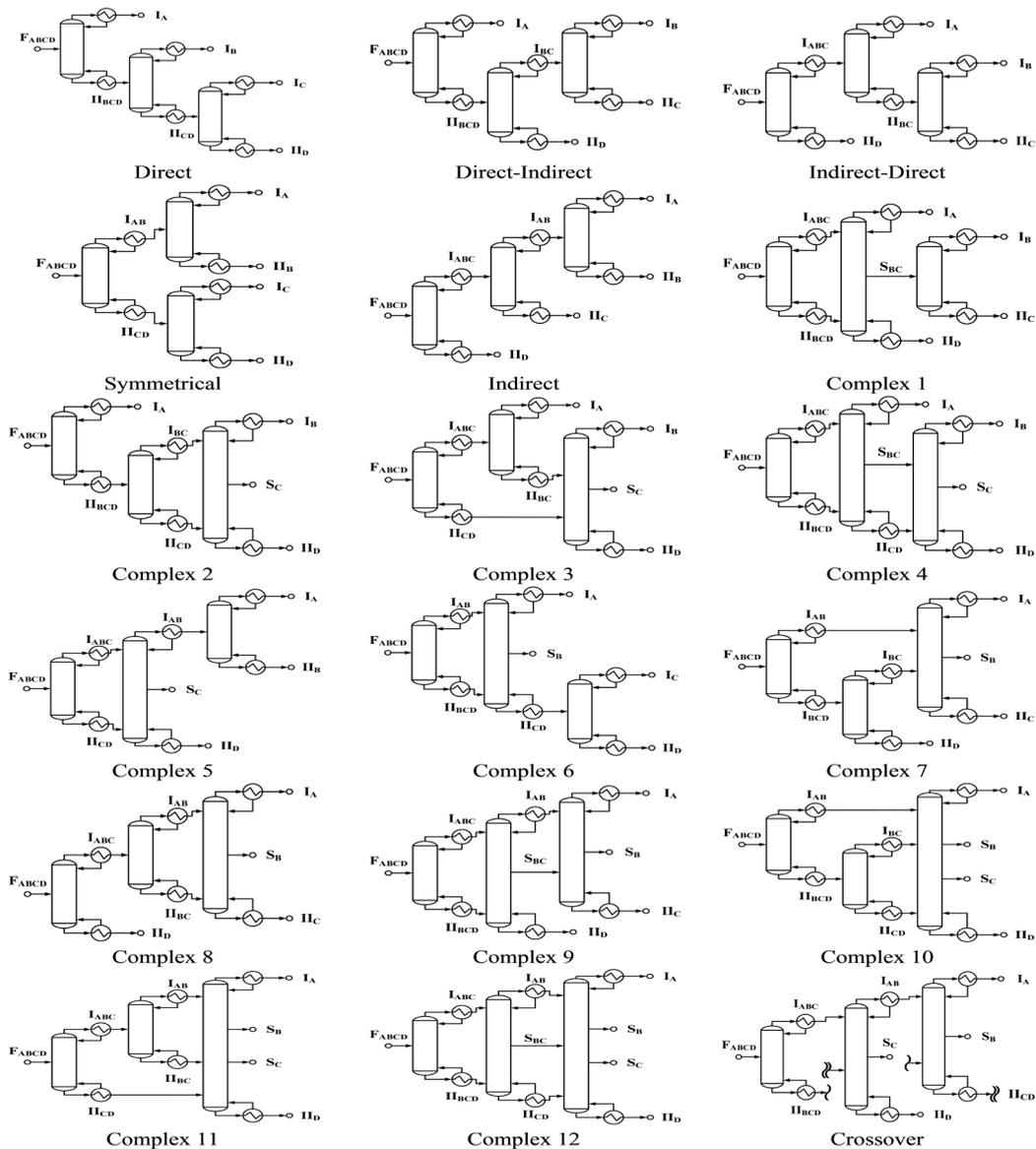


Figure 1. Distillation Columns Configurations for Four-Component Systems

4. Results and Discussions

The columns operating pressures are calculated by heuristic and stochastic methods for all simple and complex distillation scenarios. The TAC function is calculated for each sequence in the optimum pressure of two methods and the results shown in Fig. 2. In the heuristic method, the pressure of each column changed from atmospheric pressure (101 kPa) with a step size of one kPa to find the suitable condenser utility type. The sequence pressure is calculated simultaneously for all columns to minimize the TAC of the sequence in the GA method. The population size of the GA is 50 individuals in each generation and crossover fraction is 0.8. The results of the two methods for simple sequences including direct, direct-indirect, indirect-direct, symmetrical and indirect are reasonably similar. In the complex

sequences, some of the calculated pressures by the two methods are different. These lead to different TACs. In all cases, the TAC of the GA is less than or equal to the heuristic method result. The largest differences are observed in Complex4, Complex9, Complex11, Complex12 and Crossover sequences. The computational time for each sequence in the heuristic method has been one-sixth of the genetic algorithm.

The difference between this two algorithm results might affect sequences rankings and the shortcut simulation cannot indicate the best sequence globally but the rigorous simulation and optimization results of this process demonstrates the Complex2 sequence is de best distillation configuration for NGL fractionation process (Tamuzi et al. 2020).

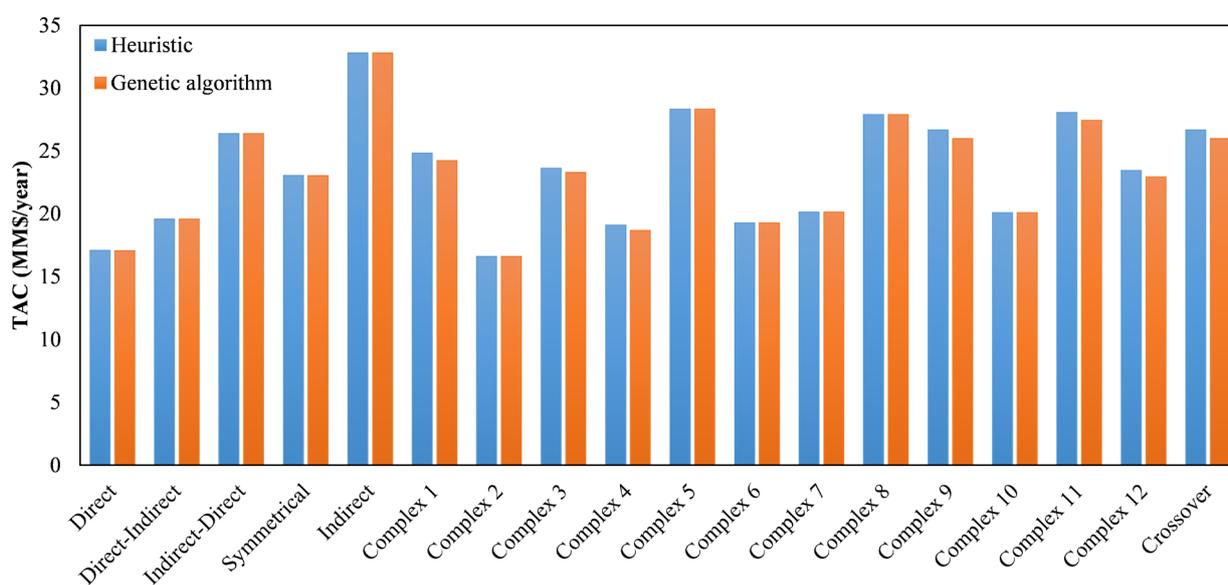


Figure 2. The Calculated TAC from Heuristic and Genetic Algorithm Methods for Distillation Sequences

The Complex9 sequence is illustrated in Fig. 3a. The calculated TAC for this sequence by the heuristic method is 3% greater than GA results. Fig. 3b shows the columns operating pressure of this sequence. The second and third columns pressures are the same in two methods. For the

first column, the heuristic algorithm has been stopped in 1650 kPa but the GA has chosen 2860 kPa as optimum pressure. A closer look at the effect of the first column's operating pressure on the column and the configuration performance has been made.

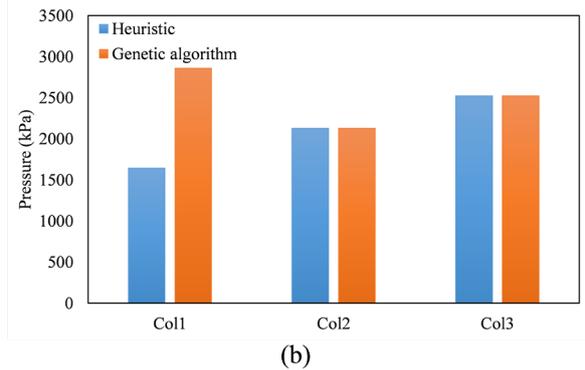
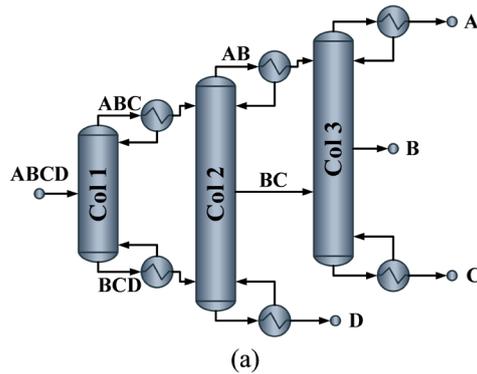


Figure 3. The Sequence with Highest Error (a) and Calculated Column Pressures by Two Methods (b)

The first column (Col1) of the sequence shown in Fig. 3a is used as a pre-flash column to separate all of A component with a part of B, C components as non-sharp distillate stream and all of the condensates (D) with a part of B, C as non-sharp bottom product. The Col1's products are the feed streams of other columns of the sequence. The impact of this column operating pressure on the condenser and reboiler temperature is shown in Fig. 4. The dotted lines illustrate the temperature of each utility which can be used as heating or cooling proposes in the reboiler and condenser. The low-pressure steam can be used in reboiler for all of the pressure range, but the condenser utility is interdependent to the column pressure. Increasing the column pressure increases the condenser and reboiler temperature and makes possible using the inexpensive utility in the condenser. Because of the non-sharp separation in the Col1, the reboiler temperature is always lower than low-pressure steam but for the separation of heavier hydrocarbons, the trade-off of reboiler and condenser temperature is more important in economic optimization.

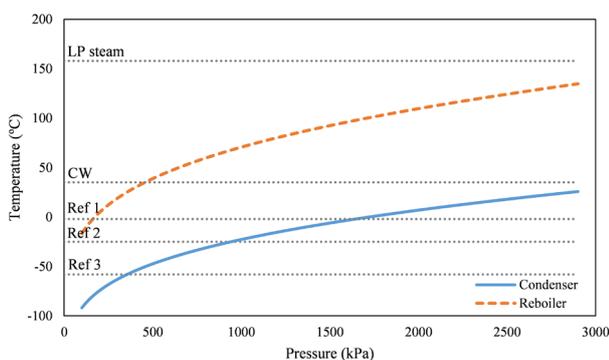


Figure 4. The Impact of Col1's Pressure on Condenser and Reboiler Temperatures

The shortcut design of distillation column utilizes the thermodynamic equations to estimate column operating and geometry. Accordingly, the column pressure affects components relative volatilities and the number of theoretical stages, minimum reflux ratio and so on. The effect of the column pressure on reflux ratio for Col1 is shown in Fig. 5a. Increasing the column pressure from atmospheric pressure to 420 kPa decreases the reflux ratio and then increases until 2860 kPa. Increasing the reflux ratio changes the column internal flow rates and the vapor flow rate directly affects the column diameter but as seen in Eq. 6 the column diameter inversely changed with pressure. The impact of the pressure on the column diameter is shown in Fig. 5b. This trade-off, cause the minimum column diameter at 2520 kPa. Another important parameter in the distillation column design is the number of stages. As shown in Fig. 5c, the number of actual stages of the same separation, increases with column pressure. Considering all of these parameters, the column capital cost increases with operating pressure.

The NGL fractionation unit is an energy demanding distillation process and a major part of the TAC belongs to the unit operating costs. Fig. 5d shows the impact of column operating pressure on the annual operating cost. From atmospheric pressure to 1650 kPa, the capital cost decreased with the increase of the pressure, but then the capital cost mildly increased. According to the results and considering the first column, the best operating pressure of this column is 1650 kPa. The heuristic method shows the same result

for this column as the best operating pressure. In 1650 kPa, using the inexpensive utilities is possible, the operating cost of Col1 is minimized and the capital cost is as low as possible at

pressures greater than 1650 kPa. However, as the main objective of this research, the operating conditions of a column may affect the entire unit and this should be investigated.

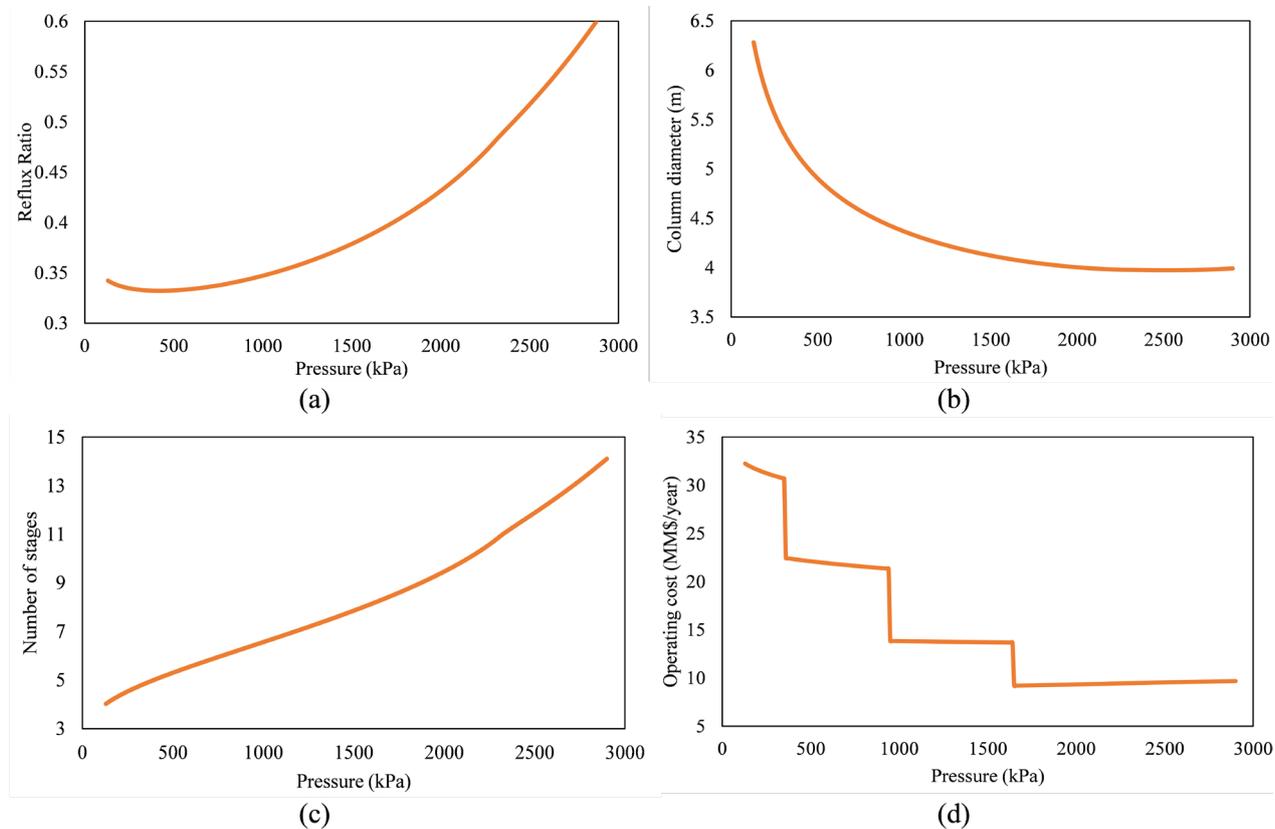


Figure 5. The Impact of the Col1's Pressure on the Reflux ratio (a), the Column Diameter (b), the Number of Stages (c) and the Column Operating Cost (d)

As it mentioned the columns of a distillation sequence are not independent, and the columns interplay effects are more in complex configurations. TAC as a comprehensive objective function can be useful in investigating the effect of operating conditions on the distillation unit economy. Fig. 6 shows the impact of the operating pressure of Col1 from Fig. 3 on the TAC of that column and whole sequence. Increasing the pressure decreases the TAC of the Col1 and the sequence until 1650 kPa. After that, the Col1's TAC starts to increase from 9.38 MM\$/year at 1650 kPa to 9.92 MM\$/year at 2860 kPa but the sequence shows different behavior and the TAC increased 0.5 MM\$/year with increasing the pressure. This happens because increasing the column pressure increases the column products temperature those are the feed streams of the

next columns. Increasing the temperature of the middle streams can reduce the cost of other columns and compensate for the increase in the cost of the first column.

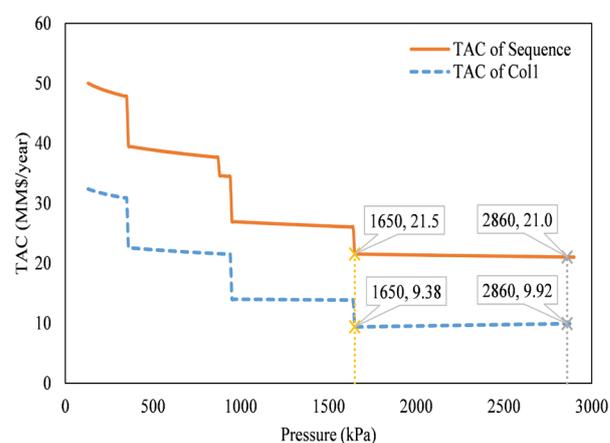


Figure 6. The Impact of the Pressure on the TAC of the First Column and the Sequence

5. Conclusions

The energy consumption and environmental pollutions subjects are so important in petrochemical upstream units like NGL fractionation plants. Using innovative designs instead of conventional processes may be useful and improve the operation of the unit. The design of these processes is more complex and need to use computer-aided simulation, optimization and design methods. For this purpose, this research investigates the impact of columns operating pressure on the plant operation and economy. The two methods of heuristic rules and stochastic optimization for the design of simple and complex distillation configurations of the NGL fractionation process are compared.

Simulation of distillation sequences is carried out by aspen plus shortcut columns and the Matlab used as the optimizer for manipulating the simulator by Aspen-Matlab linking method. The results illustrate the heuristic method can be used as a quick calculation in simple configurations, but in complex distillation sequences have some errors against stochastic optimization results. In the studied case of the NGL fractionation process, the calculated column pressure by a heuristic method showed up to 40% different in comparisons against stochastic optimization results. This error leads to a 3% increase of the total annual costs in the heuristic method, which may have a significant impact on the final design and change the evaluation distillation scenarios because of cumulative error effects.

Appendix A

Aspen and MATLAB linking methods (Example code)

```
Aspen=actxserver('Apwn.Document.36.0');
Aspen.invoke('InitFromArchive2','C:\Users\***.apw');
Aspen.visible=1
Aspen.SuppressDialogs=1;
Run2(Aspen.Engine);
for P=P0:P
```

```
Aspen.Application.Tree.FindNode('\Data\
Blocks\B1\Input\PRES').value=P;
Run2(Aspen.Engine);
X(i)=Aspen.Application.Tree.FindNode('\Data\
Streams\2\Output).value
Calculate TAC
end
```

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JOURNAL OF GAS TECHNOLOGY

Volume 7 / Issue 1 / Summer 2022 / Pages 14-35

Journal Homepage: <http://jgt.irangi.org>

Identification of Key Quality Attributes in Gas Pipeline Transmission Projects Using Repertory Grid Method

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ARTICLE INFO

ORIGINAL RESEARCH ARTICLE

Article History:

Received: 2 July 2022

Revised: 10 August 2022

Accepted: 21 September 2022

Keywords:

Quality attributes

Construct

Repertory grid

Cluster

Gas transmission

ABSTRACT

The purpose of this study is to identify the key quality attributes in gas transmission projects.

By applying Kelly's personal constructs theory and repertory grid methodology as well as conducting interviews with 20 managers and experts of gas transmission projects, as many as 284 quality constructs have been identified. These constructs were classified into 40 categories by using content analysis, and they were subsequently analyzed with statistical methods. By applying the statistical analysis nine quality attributes include, compliance with the standards, competence, appropriateness in design and engineering, effective supervision, sound execution, desirability, convergence, accountability and integration were identified. These construct as the main factors affecting the quality of gas transmission projects.

In this study, the data were collected from the gas transmission projects conducted from the employer's departments. The subsequent studies not only increase the number of interviewees but also apply the contractors' participation in the interviews to have more comprehensive results. Given the conditions of volume, temperature, and pressure, oil industry projects are of critical sensitivity and significance. The managers of project-oriented organizations can apply the findings of the present study to promote project quality and success.

The present study is an original one; it is one of the main issues to be studied in investigating the concept of quality in gas transmission projects. This study includes the experimental evidence regarding the positive effect of quality attributes on the performance of such projects. Moreover, the present study attempts to develop the related literature on quality.

DOR: [20.1001.1/JGT.2022.556487.1003](https://doi.org/10.1001.1/JGT.2022.556487.1003)

How to cite this article

M. Chegeni, R. Noorossana, S. Noori. Identification of Key Quality Attributes in Gas Pipeline Transmission Projects Using Repertory Grid Method. Journal of Gas Technology. 2022; 7(1): 14 -35. (http://jgt.irangi.org/article_255123.html)

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Available online 22 September 2022

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1. Introduction

The global-scale construction sector is the basic industry on which the development of a country depends on. A country development status is generally determined by the quality of its infrastructures and construction projects (Wasiu et al., 2012). However, the construction industry has been criticized over the past decades for its poor performance and efficiency (Loushine et al., 2006). As clients in this industry move forward and seek improvements in service quality, the continuous improvement in the concepts of quality is strongly dependent on group culture and collaboration at internal and external organizational levels. Problems, such as the poor quality of performance, inattentiveness to workplace and manpower, as well as rework costs have led to the creation of a quality management system in the construction industry (Gandolfi et al., 2001). It has also been reported that quality is one of the most effective factors in the success of construction projects (Mane & Pati, 2015). Accordingly, the quality and success of construction projects could be considered as meeting the expectations of project participants so that upon client satisfaction, long-term competitiveness and survival are achieved for commercial companies (Tan & Abdul-Rahman, 2005).

Given the large amount of research done on this topic, it is observed that quality has been developed extensively in repetitive operations, such as goods and services, but it has been left in the study phase in projects. It is clear that some attributes, such as beauty and efficiency must be utilized to describe quality because different people perceive them differently. Therefore, attributes could be defined as the aspects of the product itself or its use, which are based on the comparison of the product alternatives (Grunert, 1989). According to Müller et al. (2007), research shows that projects vary in different industries, and quality attributes are varied (Curkovic et al.,

2000). Thus, there is a research gap in the field of gas transmission pipeline projects, where quality is required to be studied. This article is organized to examine the relationship between quality and projects. Initially, project attributes as well as quality attributes in products, services, and projects, in addition to the application of these attributes in construction projects are discussed. Next, the research methodology is explained. Results from the analysis of the findings are presented in the next part. Finally, the key findings of the research as well as opportunities for new studies are provided and summarized concerning the practical implications of the results.

2. Literature Review

2.1. Project Attributes

Although projects vary in size, theme, and nature, they share common attributes. The recognition and awareness of these attributes could be effective in identifying quality attributes in the project environment. Attributes, such as change (Geraldi et al., 2009; Sun and Meng, 2008), ambiguity (De Meyer et al., 2002), uncertainty (Huchzermeier and Loch, 2001; Sun and Meng, 2008), uniqueness (ISO 10006, 2003, Forsberg et al., 2000), temporariness (PMBOK, 2008), integration (Ancona and Caldwell, 1990; Ford and Randolph, 1992), dynamicity (De Meyer et al., 2002), novelty (Turner 1999), complexity (Baillet et al., 1994; Pich et al., 2002), context-centeredness (Vidal et al., 2011), and intangibility (Pitsis et al., 2003; Winch and Kreiner, 2009) have been introduced as project characteristics emphasized by researchers in this field.

2.2. Quality Attributes in Products and Services

The word quality is often associated with different meanings for different people. Quality is both an objective and a subjective term, for which individuals have their own definitions. It could be examined from a variety

of perspectives (ASQ Glossory, 2008). According to Reeves and Bednar (2004), quality is easy to imagine but difficult to define. However, researchers in the field of quality have provided different definitions for it, with every of whom having considered a particular attribute for it, including fitness for use (Juran, 1998), meeting customer expectations (Kano, 1984), fulfillment of requirements (PMBOK, 2008, ISO, 9000: 2005), competency (Juran, 1974), reliability, usability, price, serviceability, availability, and security (ANSI / ASQC, A3-1987), degree of excellence (Hoyle, 1998), satisfaction (Hoyer & Hoyer, 2001), as well as attributes and design (Curkovic et al., 2005), which have been described in products and services.

2.3. Quality Attributes in Projects

In a research titled 'identifying key success factors in project performance', factors such as competence, communication, effective quality assurance, compliance with standards, as well as positive attitude and durability were introduced (Homthong & Mounnoi, 2004). Likewise, Geraldi et al (2011) introduced the attributes of commitment in quality, empowerment, completeness, clarity, integration, adaptability, meeting requirements, compliance, and the value added aimed at developing the concept of quality in the field of information technology projects. Karna (2004) pointed out to the attributes of competence, abilities, capability, confidence, and loyalty in analyzing customer satisfaction and construction quality.

Hamzah et al (2010) considered professional ethics as an important human factor in improving quality in construction projects. Arazi & Mahmoud (2010), in a research titled 'a framework for contractor qualitative assessment in construction processes', emphasized conformance to quality standards in the fields of materials, labor skills, equipment, and methods in construction projects. El-Mikawi (2002) considered sustainability as a factor effective in the success of construction

projects, which is achieved by examining and evaluating different concepts of sustainability in the life cycle of projects. Tai et al (2016), in examining factors affecting the trust between contractors and the owners of construction projects, identified 24 trust attributes, some of which being sharing information, communication, competence, reputation, integrity, and opportunistic behaviors.

2.4. Application of Quality Attributes in Projects

Nowadays, upon the development of the concept of quality in goods and services, its application in projects has been expanded as well. In this regard, Slack et al (2004) believe that a project could be the combination of services and goods. In the following sections, some of the applications of quality attributes in projects will be provided.

Humphreys (2004), Towler and Sinnott (2008), and Dysert (2006) have applied accuracy attribute for describing the cost estimation of different activities of construction projects. Accuracy is a degree showing the deviation from the real price. In terms of the completeness attribute, Yates and Hardcastle (2003) have referred to the perfectness of the contract and project documents. However, Cho and Gibson (2001) have referred to the perfectness of the project definition. According to Ganaway (2006), conformance to quality standards is the capability of creating the requirements in construction industry.

The companies acquire the credibility attribute through a variety of activities including social, technical, commercial, and operational activities (Rehme and Svensson, 2011). According to Jiang et al. (2011), believability and reliability are associated with credibility. They have also indicated that credibility indicates that the parties have managed to fulfill their promises.

Responsiveness attribute is the ability to respond to the changing condition and

interactions with the customer. According to Reis et al. (2004), responsiveness is a main marker in the safety of relationships.

The deliverables are either goods or services that can be tangible or intangible (Kermit Burley, 2013). The tangibles include documents, reports, software products, building, or server updating that can be effective for controlling and ensuring the efficient management of the companies (Cutting and Thomas, 2009).

Another important factor in a given project is timeliness that can affect the success or failure of a project (Hai et al., 2014). According to Michnik and Lo (2009), timeliness refers timely execution of the affairs without any delay. This attribute emphasizes the completion of a contract at the scheduled date. Evans and Lindsay (2005) have defined accessibility and convenience as the ease in conducting contract services.

According to Parasuraman, Zeithaml, and Berry (1985), security can be defined in physical and financial issues and the confidentiality of the project.

3. Material and Methods

3.1. Personal Constructs and George Kelly's Theory

Personal constructs theory was first introduced in the field of psychology by George Kelly in 1950. Kelly (1995) stated that everyone has a set of personal constructs and the constructs indicate our expectations from the events. Therefore, it was attempted to highlight the active nature of the constructible structures (Sokkia, 2007). Kelly (1995) attempted to study individuals and the psychological processes of each person's interpretation from the outside world (Ma and Norwich, 2007). The personal constructs theory discussed by Kelly (1995) is based upon the metaphor "knowledgeable human"; this theory considers a dynamic and active role for human in creating knowledge

(Niu and Easterbook, 2007). Each individual's personality consists of an organized system of constructs that are likely to be classified based upon their significance (Jankowicz, 2004). In confirming this theory, Fransella (1972) states that people interpret their physical and social affairs in a specific way and create a pattern in this way. People predict the events, individuals, and themselves based on the patterns and they use such patterns to guide themselves. Thus, it is required to understand people's structural patterns.

Personal constructs theory was first introduced in the field of psychology by George Kelly in 1950. Kelly (1995) stated that everyone has a set of personal constructs and the constructs indicate our expectations from the events. Therefore, it was attempted to highlight the active nature of the constructible structures (Sokkia, 2007). Kelly (1995) attempted to study individuals and the psychological processes of each person's interpretation from the outside world (Ma and Norwich, 2007). The personal constructs theory discussed by Kelly (1995) is based upon the metaphor "knowledgeable human"; this theory considers a dynamic and active role for human in creating knowledge (Niu and Easterbook, 2007). Each individual's personality consists of an organized system of constructs that are likely to be classified based upon their significance (Jankowicz, 2004). In confirming this theory, Fransella (1972) states that people interpret their physical and social affairs in a specific way and create a pattern in this way. People predict the events, individuals, and themselves based on the patterns and they use such patterns to guide themselves. Thus, it is required to understand people's structural patterns.

3.2. Repertory Grid

Understanding people's mentality and extracting personal constructs call for special tools. One of these tools is George Kelly's

repertory grid that has been created based on in-depth construct interviews and laddering technique; it is resulted from the interaction made between the interviewer and the interviewee. Repertory grid technique is used in cases where the researcher intends to know how the individuals understand the world and how they apply their own mental constructs to give meaning to the phenomena especially the complicated issues with any possible bias (Partington, 2002). One of the reasons for the popularity of the repertory grid technique is its three major advantages over other quantitative and qualitative techniques, which include the ability to determine the relationship between constructs, ease of use, and the lack of scholar bias. Separate networks allow for providing precise definitions for concepts and the relationship among them (Boyle, 2005).

In this study, 20 managers and executives experienced in gas transmission pipeline projects were interviewed to collect data from the repertory grid using structured partnership-based interviews (Jankowicz, 2004). The interviewees had a bachelor's degree and beyond it, with 80% of them having had more than 20 years of experience.

In the present study, a repertory grid composed of a collaboration-based structured interview was used for collecting the data (Jankowicz, 2004). The process of conducting the interviews and the formation of the repertory grid consists of three main steps: 1. Selecting the title and elements; 2. Extracting the constructs; and 3. Connecting the elements to the constructs (Tan and Hunter, 2002).

3.2.1. First step: Selecting the Title and Elements

A repertory grid is based on what we are trying to understand. Since the present study aims at understanding the quality of projects, the repertory grids are based upon quality in the projects. In repertory grid method, the elements

are specific objective examples covering the domain of the research subject (Tan and Hunter, 2002). The elements used in the repertory grid can be anything and it completely depends on the investigated concept. According to Jankowicz (2004) and Anderson (2007), there are 6-12 favorable elements for a repertory grid. In the present study, by using the "role titles method", as many as 6 locations were determined as the elements for describing quality in gas transmission projects. These elements include:

- The highest quality gas transmission projects;
- The lowest quality gas transmission projects;
- The high quality gas transmission projects;
- The low quality gas transmission projects;
- The average quality gas transmission projects;
- The ideal quality gas transmission projects.

3.2.2. Second Step: Extracting the Constructs

After selecting the elements and placing them in the repertory grid, the next step is to extract the constructs belonging to each person through making a systematic comparison of elements with each other. The most important attribute of a construct is its bipolarity (Fransella, 2004). Thus, bipolarization is an essential factor for understanding and extracting the individuals' mental constructs (Marsden and Littler, 2000). Von (2009) introduced dual and triple extraction methods as the main approaches for extracting the constructs. Moreover, during the interviews, upward and downward laddering techniques can be also used for ensuring a better and more accurate understanding of the constructs and their details. According to Tan and Hunter (2002), as many as 15-25 individuals are appropriate for acquiring the required constructs.

For collecting the data, the interviews were conducted on 20 experienced managers and officials involved in gas transmission projects. All of the interviewees had at least undergraduate

degrees and 80% of them had a working experience of 20 years and more.

In the present study, the contrast-based dual method was applied. The two elements were provided and the interviewee was asked "How are these two elements similar or different from each other?" If the interviewee refers to their differences, the differences will indicate two poles of the construct. However, if interviewee refers to the similarities, the interviewee is asked to point out the opposite of that similarity. The interview was conducted to the saturation point i.e. the interviewee failed to provide a new construct.

3.2.3. Third step: Connecting the Elements to the Constructs

In this step, each of the elements are analyzed and evaluated based on each bipolar construct; it will be clear how individuals describe each element based on a given construct and differentiate the elements (Rogers and Ryals, 2007). Thus, after selecting the elements and extracting the personal constructs, it is essential to connect the elements to the constructs. For making a more accurate distinction between the elements (based on the construct) and providing an opportunity for reflecting the participants' impartial views, a grading method is applied for evaluating the elements. Five-point or seven-point scales are the most common scales used in most of the studies (Von, 2009). In evaluating the elements of the present study, the five-point Likert scale was used for reflecting the participants' impartial views.

The reliability of the repertory grid has made it attractive not only for repeating the same results but also for showing change or stability and whatever they imply (Fransella et al., 2004). Fransella and Bannister (1977), in reviewing some studies on the repertory grid, expressed that high or low reliability was not important; according to them, what mattered was that if individuals maintained or changed their

interpretations of events, the network would be capable of representing them. In the repertory grid, network validity is determined by its ability to make individuals know how to describe their own interpretations (Petersen, 2004). From this perspective, a network able to reflect a more accurate description of people's interpretations will have higher validity (Fransella et al., 2004).

Similar to the study conducted by (DanaeeFard et al., 2014), the following measures were adopted to ensure the reliability and validity of the findings in this study:

- Using the role title or role description method at the element selection stage
- Using the ladder complementary method at the construct extraction stage
- Matching the extracted constructs using the participants' viewpoints at the extraction stage
- Using a 5-point Likert scale at the stage of connecting the elements to the constructs
- Performing a content analysis by the researcher as well as two project management experts

4. Results

By conducting 20 independent interviews, as many as 20 unique repertory grids were formed and 284 personal constructs were extracted. Since the number of the constructs obtained was too many to be analyzed, the constructs were added up and combined by using content analysis technique. Similar constructs were categorized in 40 groups forming the secondary constructs (See Table 1).of small foot print in skid design, the SMR process with one phase separator (by 43% sharing in SMR processes) has been selected in this paper. The commercialized liquefaction units by companies such as Linde, Black & Veatch, Air Products and so on, also contains only the 0-phase, 1-phase and 2-phase separators in their refrigeration cycles.

Table 1. Secondary Constructs Obtained from the Content Analysis

ID	Secondary Constructs	Frequency Initial Constructs	Description of the Positive Pole of the Secondary Construct
1	Compliance with the standards- nonconformity with the standards	13	Adhering to the basic requirements defined for the products in terms of quality, health protection, consumer's safety, and environment
2	Competence-incompetence	18	Having the required expertise, experience, and financial ability
3	Appropriate design and engineering- inappropriate design and engineering	12	Having the designing capability as well as basic and detailed conceptual engineering
4	Effective supervision - ineffective supervision	18	Enjoying a systematic procedure for ensuring the execution of plans, correct use of resources, and achievement of goals
5	clarity- ambiguity	7	Enjoying a management based on clarity of goals by justifying the human resources about their duties and responsibilities
6	flexibility- stiffness	11	Enjoying the organizational capabilities for managing the required changes in designing and engineering, structure, human resources, and merging/combining processes and working methods
7	Commitment- indifference	6	Commitment to a project and the duty or warranty existing for a project
8	Sound execution- unsound execution	6	Adherence to the initial studies and the feasibility report of the project, selecting competent contractor and consultant, and clarity of the deliverables in engineering documents
9	Specialization-generalism	13	The presence of well-informed expert staff in an organization regarding the subject of the project and their own responsibilities, accurate classification of essential duties and principles by the individual
10	Technology oriented- traditionalism	10	Applying technology and new construction method for speeding up the construction process, reducing the execution time, and promoting the intended quality
11	Desirability- undesirability	6	The set of product attributes in terms of quality and quantity that brings about an admired product
12	Convergence-divergence	17	Enjoying the cooperation between different units or parallel activities for common goals
13	Accountability- unaccountability	11	Responsibility, accountability, and acceptance of a project requested from an individual

14	Continuity-Discontinuity	18	Continuity is a fact of something continuing of existence or operation for a long period of time without being changed or stopped (continuity of developers' key resources on their project)
15	Duplication- induplication	6	Adherence to the principles of project execution for reducing the unwanted duplication within a system
16	Satisfaction- dissatisfaction	5	The project employer's feeling or attitude toward the project or project services after its operation
17	Underuse- overuse	2	The highest efficiency is achieved by using the least energy possible
18	Supplying the requirements- failure to supply the requirements	6	The needs and expectations of the employer or the beneficiaries are fulfilled
19	Integration- separation	13	Enjoying a sound background for registering and recording the uniform and compatible information for using in the systems or fulfilling the needs
20	Empowerment- weakening	6	Enjoying a process in which the individuals are able to control themselves and take up new responsibilities
21	Objectivism- subjectivism	4	Enjoying an objectivism independent of beliefs and attitudes
22	Effective communications- ineffective communications	8	Supplying an appropriate network and required data for all of the key factors needed for the execution of a project
23	Foresight - presentism	2	Understanding the possible future opportunities and selecting them for directing the present measures
24	Participation - isolation	4	The individuals' mental and emotional involvement for achieving the intended goals
25	Safety- risk	5	Adherence to principles that reduce the rate or degree of risk
26	Reliability- unreliability	4	Enjoying the likelihood of an accurate function for a definite time (based on the existing and predetermined condition)
27	Efficiency- waste	4	The capability of achieving the defined goals
28	Time management- time mismanagement	3	Enjoying the processes required for the management of project's timely completion
29	Stability - instability	6	Enjoying a series of status that are required to continue over time
30	Cost retrenchment - cost overshoot	3	Continuous improvement of value-adding activities and reducing or excluding non-value-adding activities

31	Team oriented- individualism	7	A group of individuals that bring about synergy for achieving a definite goal by having complementary skills
32	Risk management- risk mismanagement	2	A systematic method for excluding uncertainties so that the system increases the likelihood of achieving the goals
33	Good documentation- bad documentation	3	The project's deliverable documents are complete, adequate, and accurate
34	The architectural beauty of facilities (nice) - the architectural ugliness of facilities (unlikable)	3	The harmony and coordination of equipment and facilities with the arrangement of spaces and environment
35	productivity- idleness	3	The execution of activities with the least resource waste
36	added Value - added loss	2	Enjoying a profit beyond the initial expectations of the investor in a specific field
37	Creativity and innovation - inability	4	Enjoying mental capabilities for creating a new idea or concept
38	Dynamism- staticity	3	The organization's alignment with environmental changes and creating the possibility for predicting results and effects of managerial decisions
39	Accessibility- inaccessibility	5	Ease of operating, repairing, checking, and supervising the equipment and having access to the equipment
40	sustainability- unsustainability	5	Giving due attention to effective environmental factors in places people live

When the content analysis was conducted and the constructs were classified in 40 categories, the repertory grid was formed. This grid is a rectangular matrix in which the element grading was conducted for 40 secondary constructs; the positive and negative poles of this matrix are located on both sides of this matrix (See Table 2). As it can be seen in the matrix, the attributes of projects with a higher quality are at the positive pole. They include compliance with the standard, competence, and appropriate design and engineering. Nonconformity with the standards, incompetence, and poor and inappropriate design and engineering are all at the negative pole. According to the interviewees, ideal quality projects are the best ones, and constructs including compliance with the standards and competence have been evaluated at a very high level.

4.1. The Compliance of the Constructs

In investigating the compliance of the constructs with quality using *t*-test, it was concluded that all secondary constructs and grid elements could affect the quality of gas transmission projects. Once more,

the constructs were analyzed and investigated by the experts. The results of the binominal test indicated that according to the interviewees, most of the constructs are compliant with the measurement of the hidden attribute (the quality of gas transmission projects). However, in the re-interview, the compliance of one of the constructs was mentioned by few interviewees. Moreover, in some of the constructs, there is no reason indicating the rejection of the assumption that the number of pros and cons is equal.

Table 2. Cumulative Repertory Grid

ID	Secondary Constructs	ID	Grading	Construct (Negative pole)
1	Compliance	5	1 4 2 3 5	Nonconformity
2	Competence	4	1 4 2 3 5	Incompetence
3	Appropriateness	5	1 5 2 3 5	Inappropriateness
4	Effective supervision	4	2 4 2 3 5	Ineffective supervision
5	Clarity	5	1 4 2 2 5	Ambiguity
6	Flexibility	4	2 4 2 3 5	Stiffness
7	Commitment	4	2 4 2 3 5	Indifference
8	Sound execution	4	2 4 2 3 5	Unsound execution
9	Specialism	4	1 4 2 3 5	Generalism
10	Technology oriented	4	2 4 2 3 5	Traditionalism
11	Desirability	4	2 4 2 2 5	Undesirability
12	Convergence	4	1 4 2 3 5	Divergence
13	Accountability	4	2 4 2 3 5	Unaccountability
14	Continuity	4	2 4 2 3 5	Discontinuity
15	Induplication	4	2 4 2 3 5	Duplication
16	Satisfaction	5	1 4 2 3 5	Dissatisfaction
17	Underuse (Consumption energy)	4	2 4 3 3 5	Overuse (Consumption energy)
18	Supplying the Requirement	5	1 5 1 3 5	Failure to supply the Requirement
19	Integration	5	1 4 2 3 5	Separation
20	Empowerment	4	2 4 2 2 5	Weakening
21	Objectivism	5	1 5 1 3 5	Subjectivism
22	Effective communications	4	2 4 2 2 5	Ineffective communications
23	Foresight	4	2 3 2 2 5	presentism
24	Participation	4	1 4 2 3 5	Isolation
25	Safety	4	2 4 2 2 5	Risk
26	Reliability	5	1 4 1 3 5	Unreliability
27	Efficiency	5	1 5 2 3 5	Waste
28	Time management	4	2 4 2 3 5	Time mismanagement
29	Stability	5	1 5 1 3 5	Instability
30	Cost retrenchment	4	2 4 2 2 5	Cost overshoot
31	Team oriented	5	1 4 1 2 5	Individualism
32	Risk management	4	2 4 2 3 5	Risk mismanagement
33	Good documentation	4	2 4 2 3 5	Bad documentation
34	Nice	4	1 3 1 2 5	Unlikable
35	Productivity	4	1 4 2 3 5	Idleness
36	Added value	4	2 3 2 3 5	Added loss
37	Creativity	4	2 4 2 3 5	Inability
38	Dynamism	4	1 4 1 3 5	Staticity
39	Accessibility	4	2 4 2 3 5	Inaccessibility
40	Sustainability (Environmental)	4	2 4 2 2 5	unsustainability (Environmental)

Project with ideal quality

Project with average quality

Project with low quality

Project with high quality

The lowest quality projects

The highest quality projects

4.2. Clustering the Constructs of the Repertory Grid

The hierarchical cluster analysis was applied for clustering the constructs. The hierarchical compact method starts with single constructs. Thus, similar constructs are placed in clusters, the members of which have the highest similarity to the created clusters. The average linkage dendrogram indicates the clustering of the constructs. In the second phase, the constructs consist of 7 clusters. Figure 1 shows the dendrogram diagram.

In investigating cluster number 1, it can be seen that desirability, empowerment, effective communications, safety, costs retrenchment and sustainability constructs fall into this

cluster and the combination of this cluster with foresight construct has created a new cluster. Moreover, in cluster 3, it can be seen that competence, specialism, convergence, participation, and productivity constructs fall into one cluster for their adaptability and similarity, and the combination of this cluster with dynamicity construct has created a new cluster. On the other hand, by investigating the cluster and elements, it can be observed that projects having attributes including desirability and due attention to safety and environment are regarded as projects that enjoy a high quality in terms of their evaluation from the elements. Other cluster can be investigated just like cluster 1.

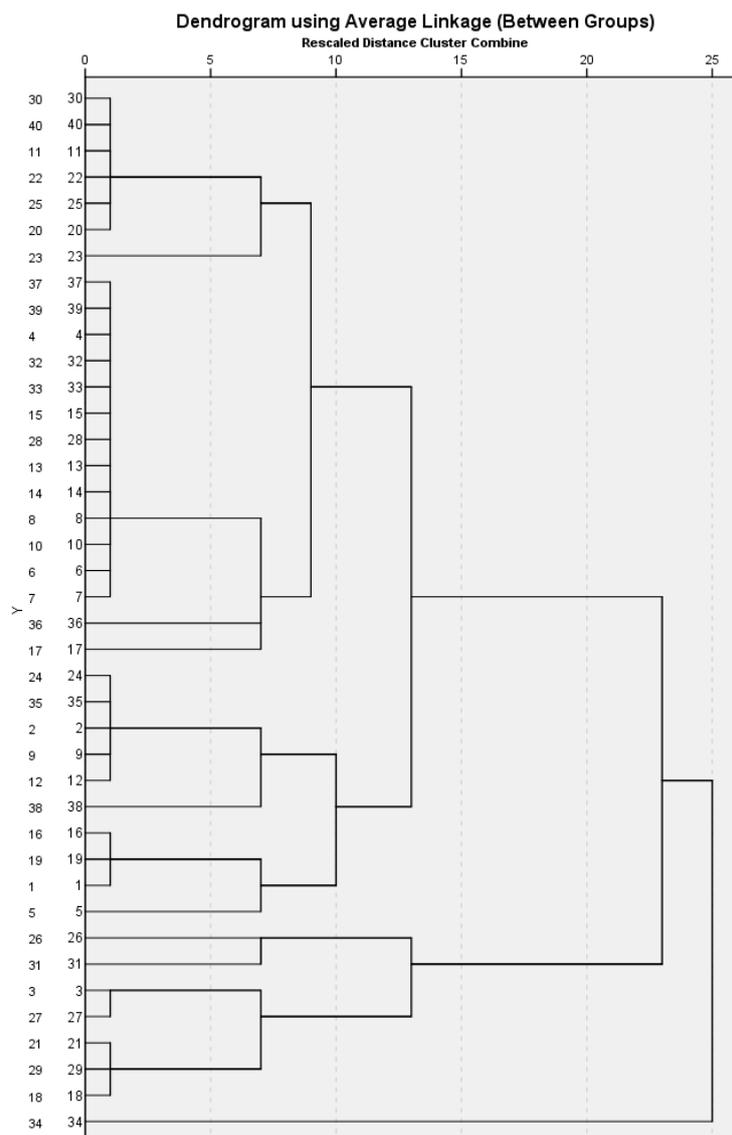


Figure 1. Dendrogram Diagram

To further evaluate appropriateness of the constructs with the related clusters, as many as 15 experts were surveyed using a questionnaire. The data were then analyzed using binominal test. After conducting the survey, most of the constructs were replaced in the suggested

clusters. Considering the significance of each cluster, cluster number 7 was excluded. This cluster consisted of only one construct, i.e. the architectural beauty of the facilities. The final clustering is provided in Table 3.

Table 3. Clustering of Constructs

Cluster	Title of Construct	Cluster	Title of Construct
1	Desirability - Undesirability Foresight - Presentism Cost retrenchment - Cost overshoot Sustainability(Environmental)- Unsustainability(Environmental) Participation- IsolationIn duplication - Duplication	4	Compliance - Non-compliance Integration - Separation Creativity - Inability Good documentation - Bad documentation
2	Effective supervision - Ineffective supervision Commitment - Indifference Technology oriented - Traditionalism Accountability - Unaccountability Continuity - Discontinuity (Consumption energy) Normally - Intensity (Consumption energy) Time Management - Time mismanagement Risk management - Risk mismanagement Added value - Added loss Effective communication - Ineffective communication Team oriented - Individualism Empowerment - Weakening	5	Reliability - Unreliability Sound execution - Unsound Execution Stability - Instability Accessibility - Inaccessibility Safety - Risk
3	Competence - Nonconformity Specialism - Generalism Convergence - Divergence Efficiency - Waste Dynamism - Staticity Productivity - Idleness Satisfaction - Dissatisfaction	6	Appropriateness - Inappropriateness supplying the Requirement - Failure to supply the Requirement Objectivism - Subjectivism Clarity - Ambiguity Flexibility - Stiffness

4.2. Identifying the Main Constructs

Pareto chart was used to identify the main constructs affecting the project quality. In the first phase, inter-cluster Pareto chart was applied to identify the cluster having the most effects on the project quality. Moreover, in the second phase, intra-cluster Pareto chart was used to identify the most important construct of each cluster using significance level of 0.05. In the first phase, the Pareto chart counter indicated the number of intra-cluster constructs. In the second phase, the Pareto chart counter identified the number of initial constructs related to each construct. They were all determined based on the

research documents.

As it can be seen from Figure 2, the x-axis indicates each of the six clusters and the y-axis shows their frequency. It can be observed that the second cluster accounts for 12 constructs out of 40 secondary constructs; it accounts for the highest percentage (30%) of the main factors. The cumulative line in Pareto chart indicates the total portion of the causes. Cluster frequency indicates that the second point of the cumulative line is higher than its previous point. Experience has shown that reducing the long bar to half is much easier than reducing the short bar to zero. Thus, if the positive pole

of the existing constructs in the second cluster improves, ignoring the other clusters will solve most of the problems related to the quality of gas transmission projects, and the quality of the entire project will improve. These factors include

ineffective supervision and control, indifference, traditionalism, unaccountability, separation, underuse, lack of empowerment, isolation, lack of time management, individualism, lack of risk management, and added loss.

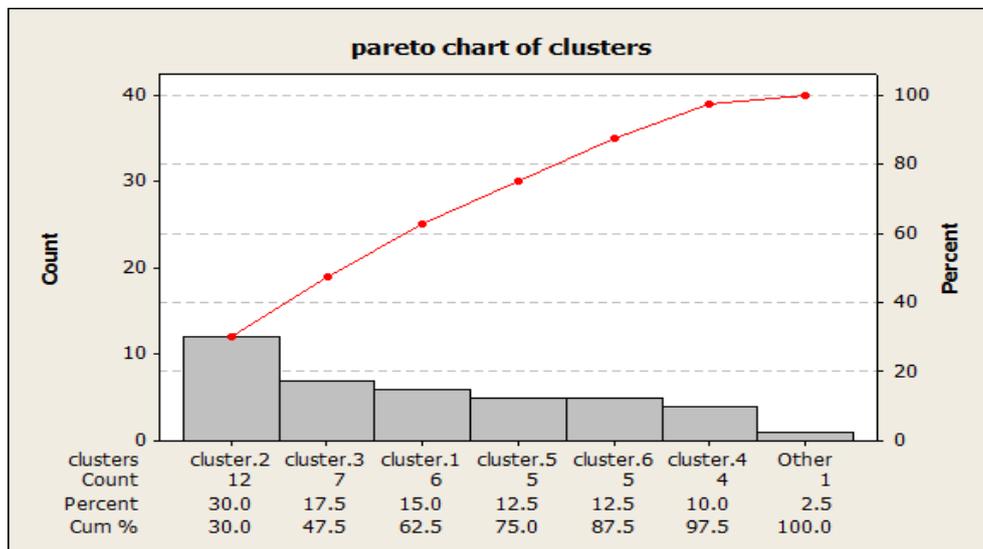


Figure 2. Pareto Diagram Between Clusters

Moreover, in Table 4 for intra-cluster Pareto chart, it can be seen that improved insignificant constructs will result in the increased quality of the project. These insignificant constructs include ineffective supervision and control, unaccountability, divergence, incompetence, nonconformity with the standards, separation, unsound execution, and inappropriate design and engineering.

The results of the first phase of Pareto analysis indicates that in comparison to the other cluster, the

second cluster accounts for the highest number of constructs with 12 constructs. Moreover, the results of the second phase indicated that constructs 4 and 13 have the highest number of initial constructs among the constructs of this cluster. The results of the second phase determined the constructs having the highest number of initial constructs in each cluster. Thus, the negative poles of the following nine constructs were identified as the main factors affecting the reduced quality of gas transmission projects.

Table 4. Pareto charts to determine the constructs of clusters within each cluster

The Title of the Negative Pole of Effective Constructs	Frequency of Construct in Primary Constructs	Num. of Cluster Constructs	Cluster Num.	Cluster
Undesirability	6	6	11	1
Ineffective-supervision	18	12	4	2
Unaccountability	11	12	13	2
Divergence	17	7	12	3
Incompetence	18	16	2	3
Nonconformity	13	4	1	4
Separation	13	12	19	4
Unsound Execution	6	5	8	5
Inappropriateness	12	5	3	6

These nine constructs account for 40% of the total 284 initial constructs. If the negative poles of these constructs are improved, most of the problems related to the quality of gas transmission projects will be solved. These attributes include:

include:

- Compliance with the standards- nonconformity with the standards;
- Competence- incompetence;
- Appropriate design and engineering- inappropriate design and engineering;
- Effective supervision/ineffective supervision;
- Sound execution- unsound execution;
- Desirability- Undesirability;
- Convergence- divergence;
- Accountability- unaccountability; and
- Integration- separation.

5. Discussion

In this section, discussion is provided based on the findings of this study and considering theoretical foundations and findings in past research aimed at investigating the degree of possible convergences and divergences.

5.1. Compliance

Technical compliance is an important attribute required for the proper performance of construction projects. According to findings (Jha, 2004), quality compliance is one of the five criteria of project performance. In the same vein, Ganaway (2006) argues that the construction industry should emphasize the need for standard-based compliance in contracting as well as in product specification, processes, and services, with everybody being required to understand it.

Therefore, the necessity of considering this attribute is consistent with the findings of other researchers in the field of construction projects.

5.2. Competence

This attribute implies project managers' qualification indicators. According to Liikamaa (2015), the literature on project management often offers various descriptive requirements, skills, attributes, and roles, with their competence being affected by personal and social attributes as well as individuals' skills. Competence has been defined as the mastering of skills and knowledge needed by all employees (Parasuraman, 1985).

Turner et al (2003) believes that competence is essential for project success but cannot guarantee project success. In contrast to Turner and Muller, Nagrecha (2002) believes that competence is an important attribute of project managers, which does not affect their leadership style and competence in project success. According to Liikamaa (2006), many competencies are shared among professional groups, but each group has also specific attributes that need to be identified according to the requirements of each organizational task. As mentioned in the present research, high-quality projects have qualified managers or contractors, with this fact being consistent with the results of other researchers.

5.3. Appropriateness

The design and engineering phase is one of the major project phases, which has been given the highest rating in the study by Sha'ar et al (2017). Babalola et al (2018) considered the purpose of the design phase to reduce losses in the construction industry in terms of time, costs, and quality. In this respect, Tang et al (2003) considers design quality as a key evaluation factor from customers' point of view, which is consistent with the findings of this study.

5.4. Effective Supervision

According to Hazir (2014), supervision involves a set of policies, methods, and tools that guarantee the achievement of project goals. In this context, Jack et al (2016) believe that the project supervision and control

process is meant to ensure that everything goes according to plans. In other words, supervision results in identifying disputes and changing management; it also updates the plans gradually according to the feedback. Hence, this attribute is in line with the results reported by researchers in this field.

5.5. Sound Execution

This attribute highlights the importance of applying the principles of project management standards as stated by the interviewees. In this regard, Chatfield (2007) describes project management as a field of planning, organizing, and managing resources to successfully achieve the project's specific goals and objectives. According to Kerzner (2005) as well as Pennypacker and Grand (2003), many studies have highlighted the benefits of using project management, for its processes could be applied in a variety of industries by providing a structured approach to successful project completion. Therefore, standard project management could be used to execute projects soundly, which is consistent with the concept of this attribute.

5.6. Desirability

This attribute represents one of the important project activities, which is the process of purchasing goods and materials as well as planning for them. As mentioned previously in this study, material management needs to be executed properly to increase project quality. According to Dakhlim and Lafhaj (2018), material management is done to ensure that the required products are provided and delivered properly and accurately at the right time and place, with the highest quality and at a reasonable price. In their findings, Khyomesh and Chetna (2011) recommended that the goods manufactured be inspected before being delivered to the site and that the requirements specified in the order be well considered. In addition, according to them, in the effective planning for purchasing, transporting, and storing materials,

the quality assurance and proper selection of manufacturers and suppliers are required.

5.7. Convergence

Convergence, in industry, is a strategic goal and a business challenge. Convergence concepts serve different purposes and functions. In addition, the convergence of human systems and technologies increases communication between people at all times and places. Alderman N. and Ivory C. (2011), in their research titled 'Translating Convergence in a Project', believe that it is necessary to examine the relationship between project convergence and divergence to determine the causes of project success and failure. In the same vein, Law and Callon (1992) stated that convergence or divergence is one of the special attributes of the actor-network relationship. Ejohwomu et al (2016) stated that conflict causes non-convergence in projects. Likewise, Acharya et al (2006) and Adnan et al (2012) stated that the lack of convergence leads to conflicts in projects, thereby making them fail. Therefore, this attribute is consistent with the descriptions presented by other studies on project failure or success.

5.8. Accountability

This attribute consists of the reliability and acceptability of responsibilities, as mentioned by the interviewees in the research process. In this study, attentiveness to trust is in line with the findings of Samuel (2001) who defined accountability as employee confidence in meeting performance commitments. It is also in line with the findings of Browning (2012) who believed that a team accepts responsibilities for the results of its actions. Accountability leads to a rapid improvement in the project process, with this being in line with the findings of McGrath and McGrath (2018). In contrast to the definitions of accountability, they considered legislative, organizational, contractual, and informal sources for accountability, which ensure a satisfactory performance.

5.9. Integration

By project integration it is meant to establish a type of interdependency among the components of an organization to achieve project goals. Since the concept of component solidarity is implied by the attribute of integration, it ensures that different elements of a project be in harmony with each other. Thus, this study is in line with the study by Baiden et al (2006) who defined integration as 'practices, methods, and behaviors, which create an effective culture of effective collaboration among individuals, organizations, and departments.' It is also consistent with the perspectives of Ibrahim et al (2011) who defined integration as the exchange of information, communication, practices, tools, and orders, which facilitates communication and interaction among team members.

6. Conclusions

Today, no one can deny the fact that project management has become quality oriented. Everyone prefers not only project delivery but quality project delivery. Therefore, quality management must be in place from the beginning of the project to the end.

In a project, quality attributes are defined by stakeholders, and a quality attribute is used to indicate how well the system meets the needs of its stakeholders. Therefore, by applying quality attributes, we can determine whether the system meets the quality requirements as well as the needs of the stakeholders.

In this study, 20 experienced managers and executives involved in gas transmission pipeline projects were interviewed using the repertory grid technique, with a total of 284 primary personal constructs of quality extracted. Next, using a content analysis, 284 primary constructs were reduced to 40, which formed a cumulative repertory grid. At the next stage, the constructs of the cumulative repertory grid were categorized into six separate clusters based on statistical similarities and using a

hierarchical cluster analysis.

In addition, by employing Pareto statistical analysis in two stages within each cluster and among the clusters, cluster representatives, including the constructs of compliance, competence, appropriateness, effective supervision, sound execution, desirability, convergence, accountability, and integration were identified and selected.

As already noted in this research, these attributes reflect the multidimensionality of quality concepts in construction projects and exhibit their different effects on quality enhancement in these projects. The study of quality in projects indicates an approach to the concept of quality in companies facing various challenges in today interactions, similar to the ones discussed here. Given these findings, continuous improvements in these attributes could be considered as important factors in meeting quality requirements in construction projects. The results of this study could be used by managers and experts in the field of gas transmission pipeline projects to improve quality management in projects by drawing upon the knowledge of important quality attributes in the studied field.

The scope of this study is limited to gas transmission pipeline projects in Iran. Methodologically, this study has limitations similar to those in empirical research. In addition, perceptual and individual bias could influence the research process in any organizations. One of the limitations of this study is the review of projects at specific times. In this study, six large gas transmission pipeline projects were studied. Bureaucracy created problems in finding project agents and conducting interviews. The interviews were long and exceeded an hour; in addition, there was always the possibility that the interviewees would get bored and not have enough accuracy in answering the questions. In addition, research should be conducted when people are emotionally prepared so as not to provide inappropriate responses under disturbing factors, such as job-related problems.

In terms of the contribution of innovation in this research, one could refer to the large number of qualitative constructs according to managers' understanding in gas transmission pipeline projects. By offering validation suggestions, this research enriches the literature on project quality; in addition, the use of these constructs by project-oriented organizations enhances the insights of managers and stakeholders. In addition, the repertory grid technique, which is based on interpretive theories, has not already been used in oil and gas projects, so it could be considered an innovation in this respect.

In this study, the quality attributes of gas transmission pipeline projects were identified by the participants. Testing and refining these attributes by further research in this field could enrich the treasury and help create new definitions for project quality. It is suggested to investigate interactions and relationships among the attributes identified in future research.

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JOURNAL OF GAS TECHNOLOGY

Volume 7 / Issue 1 / Summer 2022 / Pages 36-50

Journal Homepage: <http://jgt.irangi.org>

A Review of Application of Nanotechnology in Wastewater Treatment in Oil, Gas and Petrochemical Industries

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ARTICLE INFO

ORIGINAL RESEARCH ARTICLE

Article History:

Received: 29 June 2022

Revised: 17 August 2022

Accepted: 24 August 2022

Keywords:

Nanotechnology
Oil and Gas Industries
Wastewater Treatment
Nanomembrane
Nanoadsorbent
Nanophotocatalyst

ABSTRACT

The increase in population and the expansion of industries have led to the pollution and reduction of many natural resources, including water resources. Widespread use of these resources in domestic, agricultural and industrial uses has led to the entry of pollutants and limited water resources. One of these industries is the oil and gas industry and related sectors, such as petrochemicals, which introduce many pollutants such as heavy metals, aromatics, etc. into water sources. Therefore, it is necessary to pay attention to the correct use of these resources and strategies for treatment and reuse of wastewater. Various methods are used for wastewater treatment such as flocculation, adsorption, filtration, etc., but each of them has some limitations such as low efficiency or high cost. The use of nanotechnology is one of the solutions that has recently been considered. This method improves performance by reducing the dimension of material to nanometers. There are different types of nanomaterials that due to their unique properties such as larger surface area, ability to work at low concentrations, etc., have great potential for treating contaminated water very effectively. Studies show they can be used in various forms such as nano-adsorbents, nano-membranes, nano-filters and nano-photocatalysts to remove or reduce contaminants specially from oil, gas and petrochemical wastewater. In this review, the importance and application of nanotechnology has been discussed in wastewater treatment in oil, gas and petrochemical.

DOR: [20.1001.1/JGT.2022.559752.1010](https://doi.org/10.1001/JGT.2022.559752.1010)

How to cite this article

MR. Boskabadi, Z. Robotjazi, O.Tavakoli, A Review of Application of Nanotechnology in Wastewater Treatment in Oil, Gas and Petrochemical Industries. Journal of Gas Technology. 2022; 7(1): 36 -50. (http://jgt.irangi.org/article_696651.html)

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Available online 22 September 2022

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1. Introduction

Oil is of great importance as a national strategic resource. Oil and petrochemical production processes include various segments including exploration, development and production such as drilling, processing of hydrocarbons in refineries and petrochemicals, storage, transportation and distribution of petroleum products. Water is used in different sectors of the oil and gas industry and the resulting wastewater contains contaminants that need to be treated for release or reuse. Lack of proper treatment causes destructive effects on the environment and human health (Ahmad et al., 2020; Jafarinejad & Esfahani, 2021; Liu et al., 2021) for example oily wastewater affects on human health, drinking water and groundwater resources, air, crop production, and aquatic life (Varjani et al., 2017; Zafra et al., 2015). Also, due to the increasing shortage of usable water resources, effective wastewater treatment with safer and more efficient methods is a key priority. One promising approach that has shown growing potential, according to the results of several studies, is the use of nanotechnology (Cheriyamundath & Vavilala, 2021). Nanotechnology has been used in various industries. One of these industries is the oil and gas industry, which its applications covered different areas in upstream and downstream (Alsaba et al., 2020).

A lot of research has been done on the fabrication of nanoparticles with specific properties and applications. Nanoparticles are nanoscale versions of their bulky counterparts (Kumari et al., 2019). Nanomaterials criteria include well-organized structure, filtration capability, small in size, and high surface to volume ratio. Some special properties of materials under the nanoscale are the effects on the surface region, large quantum tunnel effects and small size effects. These properties add to their adsorption capacity and reactivity, which are unprecedented and are great for heavy metal ions removal (Basu & Ghosh, 2013; Rivero-Huguet & Marshall, 2009). The chemical, physical, optical,

electrical, magnetic and biological properties of nanoparticles make them suitable tools for removing wastewater contaminants (Kefeni & Mamba, 2020; Kumari et al., 2019; Mustapha et al., 2020).

A brief look at the recent publication related to nanomaterial reveals the application of wide range of them such as nano adsorbent for removal of crude oil and diesel oil from wastewater (Vlaev et al., 2011), nanomembrane in water and wastewater treatment (Folio et al., 2018; Khamforoush et al., 2015), nanofilters to remove biochemical oxygen demand (BOD) and total dissolved solids (TDS) (Salahi et al., 2013) and nanophotocatalyst for chemical oxygen demand (COD) removal from refinery wastewater (Saien & Nejati, 2007). Using this technology to treat and reuse effluents can be more efficient and cost-effective than conventional methods (Kumari et al., 2019).

Since the oil industry is so important and it is rapidly expanding, protecting the environment and preventing the pollution of natural resources, in particular water resources, are becoming a more prevalent topics than ever. In this review, we discuss a summary of the recent progress of nanotechnology and its successful application, especially in oil and gas wastewater treatment.

2. Nanotechnology in oil and gas wastewater treatment

Hundreds of compounds can be present in the oil and natural gas. Every crude oil type contains 200-300 different compounds. About 50-98% of the oil composition corresponds to hydrocarbons (Sayed et al., 2021), which are primarily alkanes (paraffins); 5-6 atom-per-cycle cycloalkanes (naphthenes); aromatic compounds (20-40% of the oil) such as volatile compounds (benzene, toluene, xylene), bicyclic compounds (naphthalene), tricyclic compounds (anthracene, phenanthrene) and polycyclic compounds (pyrene). In addition to hydrocarbons there are sulfur compounds reaching up to 10%, and fatty acids and nitrogen compounds, as well

as vanadium and nickel(Kharisov et al., 2014). Wastewater from the oil, gas and petrochemical industries contains many complex organic compounds such as polycyclic aromatic hydrocarbons (PAHs), aromatic hydrocarbons, oils, heavy metals, phenol, bacteria and various inorganic chemicals(Li et al., 2019; Liu et al., 2021). In addition, oily wastewater is one of the major type of wastewater discharged by different industries. The oil and gas industry produces a significant amount of oily wastewater during the exploration, production, transportation, storage, and refining of crude oils as well as the synthesis of petrochemical products. The majority of oil mixed in water is coming from petrochemical and metal processing industries, in terms of fats, hydrocarbons, and petroleum fractions like diesel oil, gasoline, and kerosene. These constituents exist in the form of oil-in-water emulsions(Abuhasel et al., 2021; Ahmad et al., 2020; Cai et al., 2020).

Nanotechnology is a science employing nanoparticle for various engineering applications including environmental remediation(Khan et al., 2019). It can be used to eliminate or reduce the pollutants. Contaminants removal from the wastewater of the oil and gas industries can be done through physical, chemical and biological methods such as adsorption, flocculation, chemical deposition, chemical oxidation and membrane filtration(Peng et al., 2020). The application of nanotechnology in these methods is effective for improving the water purification process.

2.1. Nanoadsorbent

The use of adsorbents is one of the wastewater treatment methods that has been considered due to its ease and high efficiency. Pollutants are adsorbed on the adsorbent surface, and the pores on the adsorbent surface play a key role in this process(Han et al., 2019). Therefore, specific surface area and high porosity are of special importance. The use of nanotechnology and synthesis of nanoadsorbents can increase their performance and efficiency. In addition,

nanoadsorbents can be regenerated and reused(Kumari et al., 2019). Adsorbent processes can be classified into two mechanisms of physical adsorption (physisorption) and chemical adsorption (chemisorption) according to the nature of interactions between the adsorbate and the adsorbent(Queiroz et al., 2022). Various adsorbents have been used to eliminate oil from wastewater such as activated carbon(Liang & Esmaili, 2021), lipophilic activated carbons(de Tuesta et al., 2020),etc. Recently, the use of nano-adsorbents to remove oil from emulsion has received much attention. Nano-adsorbents are broadly categorized into various groups, including metallic NPs, magnetic NPs, metallic oxide NPs ,and nanostructured mixed oxides. Also, carbonaceous nano-materials include carbon nano-sheets, carbon nano-tubes, and carbon nano-particles(Khoshkerdar & Esmaili, 2019).

Oilfield wastewater can cause several environmental problems if it is directly discharged because it contains high salinity metal ions, such as Ca^{2+} and Mg^{2+} (Imran et al., 2019; Johnston et al., 2019) Therefore, the high salinity of metal ions in oilfield wastewater, which is reinjected down to oil wells as the oil-displacing solution, can have an adverse affect on oil recovery(He, Yang, et al., 2021). Hence, effective removal of metal ions is necessary before reinjection. Graphene oxide (GO) is one of the adsorbents that are used for rapid removal of some metal ions such as Cu^{2+} due to its high adsorption capacity(He, Yang, et al., 2021). He et al.(He, Yang, et al., 2021) prepared a PEG/ Fe_3O_4 /GO- NH_2 nanoadsorbent by amination of GO, incorporating magnetic Fe_3O_4 nanoparticles, and PEG coating. The synthesized nanosorbents effectively remove Ca^{2+} and Mg^{2+} from the oilfield wastewater and displayed relatively high reusability. Also, in the core displacement experiments using oilfield wastewater treated with the nanoadsorbent, the oil recovery efficiency (11.8%) increased compared to the untreated oilfield wastewater.

In another study, He et al.(He, Wang, et al., 2021) prepared Fe_3O_4 /GO-COOH nanoadsorbents by

magnetization and carboxylation of graphene oxide (GO) to remove Ca^{2+} and Cu^{2+} metal ions from oilfield wastewater. After 30 minutes, the $\text{Fe}_3\text{O}_4/\text{GO-COOH}$ adsorption capacity for Ca^{2+} and Cu^{2+} reached 69.3% and 49.3%, respectively, and at 60 minutes reached 78.4% and 51%, respectively. In addition, after five adsorption/desorption cycles, the nanoadsorbent maintained a high recovery rate and removal percentage.

In order to remove PAHs, Ruiz et al. (Patiño-Ruiz et al., 2020) synthesized composites from chitosan beads modified with iron oxide (FeO) and titanium dioxide (TiO_2) nanoparticles via ionic cross-linking (Ch-FeO/ TiO_2). The enhanced adsorption mechanism of Ch-FeO/ TiO_2 was determined by the removal of naphthalene from water and seawater samples. The Ch-FeO/ TiO_2 showed a higher adsorption capacity of 33.1 mg/g compared to 29.8 mg/g of unmodified chitosan beads (un-Ch). Due to its cheapness and

environmental friendliness, this adsorbent can be a good option for remediation of water sources contaminated with complex compounds.

Magnetic nanoparticles have properties such as extremely large surface area per volume substance and strong magnetic response and these properties make them exciting candidates for separation applications in oil and gas production and processing. Most of the attention in application of magnetic nanoparticles has been given to the removal of dispersed oil (Lü et al., 2016; Sabouri et al., 2019). In a method to remove oil droplets from water by cationic surface-coated magnetic nanoparticles has been developed by Ko et al., Adsorption experiments were performed on a batch scale with 5 wt % decane-in-water emulsions. The reported removal efficiency of the decane droplets was in the range between 85 and 99.99 % (Ko et al., 2014; Simonsen et al., 2018).

Table 1. Nanoadsorbents samples

Nanoadsorbents	Studied Points	Results	Reference
PEG/ $\text{Fe}_3\text{O}_4/\text{GO-NH}_2$	To remove Ca^{2+} and Mg^{2+} from the oilfield wastewater	The oil recovery efficiency (11.8%) increased compared to the untreated oilfield wastewater	(He, Yang, et al., 2021)
$\text{Fe}_3\text{O}_4/\text{GO-COOH}$	To remove Ca^{2+} and Cu^{2+} metal ions from oilfield wastewater	After 30 minutes, the adsorption capacity for Ca^{2+} and Cu^{2+} reached 69.3% and 49.3%, respectively, and at 60 minutes reached 78.4% and 51%, respectively	(He, Wang, et al., 2021)
Ch-FeO/ TiO_2	The removal of naphthalene from water and seawater samples	A higher adsorption capacity of 33.1 mg/g compared to 29.8 mg/g of unmodified chitosan beads (un-Ch).	(Patiño-Ruiz et al., 2020)
Sodium salt of oleoyl carboxymethyl chitosan (NaO-CMCS) adsorbent	Enhancing the removal of oil from the creamy emulsion	75-85% oil in deionized water; 19-49% oil in seawater were recovered	(Doshi et al., 2018)
MIL-101 and MIL-101@nanoporous graphene (NPG) adsorbent	oil adsorption	The proposed composite was used successfully for adsorption of crude oil (14 g/g) in water samples	(Rahmani et al., 2018)

2.2. Nanomembrane

Membrane technology is one of the most commonly used methods for the separation of oil-water wastewater or emulsions, in food processing, pharmaceutical, desalination, and fuel cell industries (Ma et al., 2016). In recent decades, membrane technology has grown significantly due to advantages such as the possibilities of low or no usage of chemicals and environmental friendliness for use in water and wastewater treatment. With a significant reduction in the size of equipment, energy requirements and low capital costs can be a more desirable option in wastewater treatment processes.

Membrane is a barrier that separates the two phases by restricting the movement of components in a selective manner. Membrane materials are classified into two categories: organic or inorganic. Organic membranes are made from synthetic organic polymers including polyethylene (PE), polytetrafluoroethylene (PTFE), polypropylene and cellulose acetate. Mineral membranes are made from materials such as ceramics and zeolites (Aliyu et al., 2018; Obotey Ezugbe & Rathilal, 2020). Membrane separation technique used in water and wastewater treatment systems classified based on the membrane pore sizes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). MF and UF are commonly used to remove solids and/or microbes. NF and RO are used in desalination and are regularly applied for multi-valent ions (such as calcium, magnesium, sulfate, etc.) and TDS removal, respectively (Adham et al., 2018). Descriptions of membrane types with corresponding pore diameters and preserved species are shown in Figure 1. According to this figure, microfiltration can reject colloids or bacteria larger than 100 nm, ultrafiltration can reject macromolecules and proteins larger than 2 nm, nanofiltration can reject multivalent salts, and reverse osmosis can reject monovalent salts but the main advantage of nanofiltration is that they are able to work in lower pressure

(between 20-4bar) and it causes the treatment process more economical (Adham et al., 2018; Ali et al., 2019; Jafarinejad & Esfahani, 2021; Yang et al., 2019).

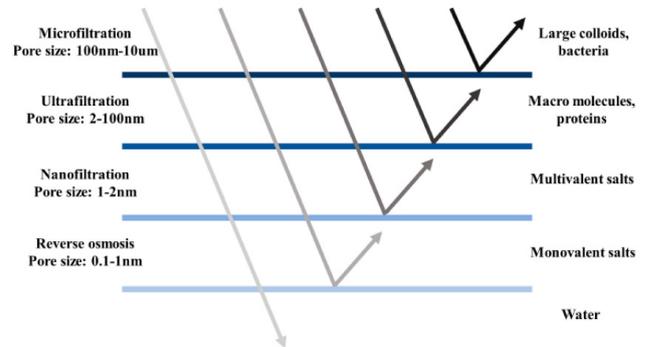


Figure 1. Classification of membranes for water purification in terms of pore size and retained species (Yang et al., 2019).

Zhang et al. (Zhang et al., 2021) prepared a new nanofiber and micro/nanospheres coated with PVDF/graphene (GE) composite membrane (TPGCM) through a simple simultaneous electrospinning/electrospray strategy. By examining the relationship between different concentrations of GE in the electrospay precursor and morphology, microstructure, wettability and performance of the composite membrane showed high permeability and excellent separation efficiency of 99.8% for the separation of different types of Span-80-stabilized water-in-oil emulsions. Velayi et al. (Velayi & Norouzbeigi, 2020) fabricated micro/nano hierarchical structured ZnO coated mesh via a simple chemical bath deposition method. The coated meshes were used for chloroform-water and n-hexane-water separations showing high efficiencies in a dead-end system. Also, the prepared meshes can selectively separate mixtures of various corrosive solutions without significant changes in flux and efficiency values. In addition, the heat-induced switchable wetting characteristics were applied to creation ZnO-mesh membranes for oil/water isolation continuously with a high permeation flux and excellent durability which is more affordable and efficient for practical applications.

Fang et al.(Fang et al., 2019) have developed a route for fabrication of catalytic-ultrafiltration (UF) membrane via blending the natural polyphenol tannic acid (TA)-Fe complexes in UF membrane matrix to in situ form Ag nanoparticles on inner pore walls of the polymeric membrane. The evenly-distributed TA provides a convenient platform for forming and immobilizing catalytic nanoparticles in the membrane matrix. As a result, most of the nanoparticles were distributed on the surface of inner pores and protected with membrane separation layer from the macromolecular pollutants. Naseem et al.(Naseem et al., 2018) prepared asymmetric composite fiber membranes of three-layered graphene oxide (GO), titanium dioxide (TiO_2) and recycled waste industrial cellulose triacetate(rTAC) to separate oil from water. GO and TiO_2 coated by electrophoretic deposition method increased water permeability on rTAC membranes. This coating can effectively repel oil and has self-cleaning and anti-fouling properties. Hu et al.(Hu et al., 2015) fabricated GO-modified MF membranes via the vacuum filtration method by using commercially alumina (Al_2O_3) as substrates. The permeate flux values of unmodified and GO-modified membranes were compared with each other, which showed 28% improvement after GO modification. Due to high electrical and thermal conductivity, as well as excellent chemical stability and mechanical strength, graphene is an excellent candidate for developing water treatment membranes(Aghigh et al., 2015). Graphene oxide has similar properties to graphene, but is more hydrophilic due to the variety of oxygen functional groups, and this property makes it better dispersible in water and other organic solvents(Noamani et al., 2019).

Nanofiltration membrane (NF) is one of the most important types of membranes used in wastewater treatment. This membrane can be aqueous or non-aqueous. The main task of NF is the selective removal of ions

and organic matter(Abdel-Fatah, 2018). The characteristics of NF which are 1- 5 nm pore size and 7- 30 bar operating pressure(Shon et al., 2013) are used to separate solutes with low molecular weight like lactose, glucose, salt, and it's effective in rejecting hardness, dye and heavy metal(Mulyanti & Susanto, 2018). In comparison with MF and UF processes, this process has higher efficiencies in the reduction of COD and TDS and also operates under low pressure (i.e., low energy usage) conditions compared to RO process(Abadikhah et al., 2015). Low energy consumption, enhanced capacity for the removal of contaminants, excellent lifetime, and cost-effectiveness have led to great popularity and wide acceptance of NF membranes worldwide(Tul Muntha et al., 2017). Nezhad et al.(Nezhad et al., 2022) investigated the performance of NF and RO membrane processes for treatment of wastewater containing ethylene glycol (EG) from South Pars Gas Complex (SPGC) and compared them. For the RO process, the EG removal from synthesized and industrial wastewaters at different pressures are 80% and 99%, respectively, and for the NF process, these are 60% and 80%, respectively, which indicates membrane technologies are suitable choices to treat industrial wastewater containing EG. In addition, it has been observed RO has better performance than NF and RO membrane has less fouling than the NF membrane, which means the RO process has more lifetime and fewer operational costs. However, it should be noticed the flux of the NF membrane is higher than RO due to less compression of the NF membrane.

Nanofiltration is increasingly used in various applications such as textile industry for separation of dyes, wastewater treatment of olive factory, removal of sulfate acid from mine water, oily wastewater treatment and etc(Mulyanti & Susanto, 2018). In Table 2, a number of studies on nanofiltration membranes are summarized.

Table 2. Nanofiltration membranes samples.

Nanofiltration membranes	Preparation method	Performance	Filtration Capacity	Reference
Zirconia nanofilter	Aqueous sol-gel process modified by glycerol	Treatment of wastewater with high salinity	At the high NaCl mass fraction varying from 0% to 24.92%, the ZrO ₂ NF membrane displays much better retention performance at about 68% while only 36% for polymeric NF membrane.	(Da et al., 2016)
Zeolite nano-particles impregnated polysulfone membranes	Nanoparticles fabricated via conventional and microwave heating methods and then incorporated into a polysulfone	Removal of nickel and lead cations	The maximum sorption capacity of the hybrid membrane for the lead and nickel ions was measured as 682 and 122 mg/g respectively at the end of 60 min of filtration.	(Yurekli, 2016)
PSf/pebax/F-MWCNTs nanocomposite membrane	The porous PSf support was prepared and then a thin layer of pebax as selective layer was coated on it	Nanofiltration of oil/water emulsion	PSf/Pebax/2%F-MWCNT membrane oil filtration value reported 99.26%.	(Saadati & Pakizeh, 2017)
Combined UF and NF/RO	The integrated membrane systems based on ultrafiltration (UF) coupled with nanofiltration(NF) or reverse osmosis (RO)	Treatment of phenolic wastewater from a paper mill	Rejections of 95.5% for COD and 94.9% for phenol	(Sun et al., 2015)
A commercial titania ceramic nanofiltration membrane	Titania Nanofiltration membrane Unit(TNU)	Reduce ion concentration, Total Suspended Solids (TSS) and Total Organic Carbon (TOC) in recycle water from a Canadian oil sands mine	High rejection of divalent cations, 75-90% TOC rejection, and almost 100% TSS rejection	(Cabrera et al., 2021)
Nanofiltration membrane (JCM-1812-50N, USA)	Thaguchi method	Removing Ba, Ni, Cr, NaCl and TDS from produced wastewater by dewatering unit of an oil and gas well drilling industry	85.3% removal of Ba, 77.4% removal of Ni, 58.5% removal of Cr, 79.6% removal of NaCl and 56.3% removal of TDS	(Hedayatipour et al., 2017)
A superwetting and robust PES-PAA-ZrO ₂ nanofiltration membrane	A ZrO ₂ coating was formed on polyethersulfone (PES) membrane surface through chemicalbonding.	Polycyclic aromatic hydrocarbon removal(PAH)	More than 90% of PAH rejection rate	(Chen et al., 2022)

2.3. Nanophotocatalyst

Among the various processes available for water and wastewater treatment, the use of heterogeneous photocatalysts is more cost-effective than other Activated Oxidation Processes (AOPs) such as ozonation or the Fenton process because of no need to addition of expensive chemicals for complete mineralization of the target compound. AOPs can completely destroy organic pollutants into carbon dioxide and water that used in the additional treatment stage, which is an optional stage known as AOPs (Gómez-Pastora et al., 2017; Hassan & Al-zobai, 2019). Some of the most widely used photocatalytic nanomaterials are Fe_3O_4 , TiO_2 , ZnO , and graphitic carbon nitride ($\text{g-C}_3\text{N}_4$). These nanomaterials and their combinations carry an enormous potential for water and wastewater treatment (Ahmed & Haider, 2018). It has been proven that the use of TiO_2 -induced semiconductor photocatalysis technology can be a suitable method for oil and gas wastewater treatment (Liu et al., 2021). since titanium dioxide has a large energy band gap (3.2 eV) which exceeds the REDOX potential of most organic compounds (Fujisawa et al., 2017), and can effectively excite oxygen and OH-radicals in water. Finally, organic matter can be completely mineralized and transformed into a carbonaceous gas, which eliminates the need of subsequent biomass treatment (Ng, 2021).

Ghasemi et al. (Ghasemi et al., 2016) synthesized a new nano- $\text{TiO}_2/\text{Fe-ZSM-5}$ photocatalyst by immobilization TiO_2 in the Fe-ZSM-5 structure synthesized by sol-gel method. The aim of this study was to photocatalytically decompose organic pollutants in oil refinery wastewater under UV and sunlight. The maximum reduction of COD was 80% at pH 4, the photocatalyst concentration was 2.1 g/L, the temperature was 45 °C and the UV exposure time was 240 minutes. In addition, the results showed that various petroleum compounds decomposed under UV and visible light and the removal of COD degradation was not reduced by increasing the photocatalyst reuse cycle.

Ethyl benzene (EB) is one of the solvents used in various fields such as organic synthesis and cleaning equipment, in addition to being used as a chemical raw material in chemical productions. Therefore, this material exists in petroleum products refinery and chemical industry wastewater. Due to improper waste disposal practices, accidental fuel spills, and leaks in underground storage tanks and pipelines may happen, EB is among the most common organic contaminants (Cui et al., 2017; Shirzad Taghanaki et al., 2021). Taghanaki et al. (Shirzad Taghanaki et al., 2021) synthesized $\text{Cu-TiO}_2@ \text{SiO}_2$ and $\text{Cu-N-TiO}_2@ \text{SiO}_2$ photocatalytic powders using three different concentrations of copper and nitrogen by sol-gel method via ambient pressure drying and the optical decomposition efficiency of ethyl benzene in aqueous media was tested under visible light. $3\text{Cu-3N-TiO}_2 @ \text{SiO}_2$ had the highest photocatalytic activity in EB degradation under visible light (90%).

Phenols in wastewater arise from a large number of industrial processes such as refineries, manufacturing of paints, pharmaceuticals, and petroleum production, are highly soluble in water, acutely toxic, and biologically recalcitrant (Maszenan et al., 2011). Phenol and its derivatives Chlorophenol and nitrophenol are broken down by photocatalytic process. The main by-products detected during its photocatalytic degradation are 4-nitrocatechol, benzoquinone, hydroquinone, and some organic acids (Maszenan et al., 2011; Ren et al., 2021). Darabdhara et al. (Darabdhara & Das, 2019) reported the colorimetric detection and photocatalytic degradation of toxic phenolic compounds using Au@Ni loaded reduced graphene oxide (rGO) nanostructures. Core-shell nanoparticles of Au and Ni are successfully designed on rGO with size < 8 nm by a solvothermal route. Additionally, the Au@Ni/rGO nanocomposite exhibits excellent photo responsive behaviour towards degradation of phenol, 2-chlorophenol (2-CP) and 2-nitrophenol (2-NP) under natural sunlight irradiation with more than 87% degradation. Khaksar et al. (Khaksar et al., 2017)

developed a novel cascade photocatalytic backlight reactor to remove phenol from petrochemical wastewater and the effect of five factors including initial phenol concentration, TiO_2 concentration, turbidity, and pH on phenol removal efficiency was investigated using full factorial design. The best removal efficiency was 88% obtained after three hours when pH is 9, initial phenol concentration equals 50mg/L, and TiO_2 concentration equals 80g/m². The significance of reaction parameters is shown as follows: time > initial phenol concentration > TiO_2 concentration > pH. The analysis also reveals that turbidity has no effect on phenol removal efficiency.

Ammonia is a common water contaminant that contains nitrogen and a source of nutrients that may accelerate the eutrophication and cause algal growth in natural water (Shavisi, Sharifnia, Zendezhaban, et al., 2014). Shavisi et al. (Shavisi, Sharifnia, Zendezhaban, et al., 2014) investigated the influence of solar light irradiation on ammonia degradation from petrochemical industry wastewater using TiO_2 /

LECA photocatalyst. The photodegradation of ammonia was performing by two methods of aeration, using air diffuser and stirring with a blender. The results showed that the ammonia removal efficiency increased with increasing the pH value. The optimal efficiency of the photocatalytic degradation process reached to 96.5%, at pH = 11. The optimum dosage of catalyst was 25 g/L which the maximum efficiency achieved with this amount of catalyst. The catalyst efficiency after three times regeneration was reduced by only about 41%. Two types of industrial aeration methods were applied in photoreactors which this comparison shows systems have almost a same efficiency on degradation of ammonia. In another study, Shavisi et al. (Shavisi, Sharifnia, Hosseini, et al., 2014) used TiO_2 /perlite photocatalysis for degradation of ammonia from synthetic wastewater, under UV light irradiation. Results showed that the TiO_2 /perlite photocatalyst after 120 min of starting irradiation removed about 64.3% of ammonia at 170 mg/L of ammonia concentration, pH = 11 and 125 W Hg lamp as UV source.

Table 3. Nanophotocatalysts samples

Nanophotocatalyst	Studied Points	Results	Reference
Vertically aligned zinc oxide nanorods (ZnO NRs) photocatalyst	Degradation of hydrolyzed polyacrylamide (HPAM) and reduction in TOC from oil and gas produced water	Reduction 51% of HPAM within 6 h, almost 20 % and 37% reduction in TOC after 7h and 14hr	(Al-Sabahi et al., 2018)
Silver/titanium dioxide/graphene ternary nanoparticles (PU-Ag/P25/G) photocatalyst	Diesel-polluted surface water	76% degradation of diesel in a period of 16 h	(Ni et al., 2016)
Ni-N-TiO ₂ floating photocatalyst	Diesel oil removal from wastewater	Diesel oil removal efficiency was 95.9% in 5 h	(Wang et al., 2017)

3. Conclusions

According to studies, nanotechnology has many applications for oil, gas and petrochemical industry wastewater treatment. The small size of nanomaterials to their bulk counterparts

has created unique properties in them. The contact surface and porosity in these materials is higher, which is an advantage in processes such as adsorption and membrane filtration.

Therefore, the separation of pollutants is done better and the effluent is treated with higher efficiency. However, it is important to mention that some of these nanomaterials are still in the stage of experimental research and there are many attempts to find a balance between economic and environmental benefits. It is also worth mentioning this point that each of these nanostructures is fitted to a specific mechanism for treating wastewater. For nanoadsorbents, pollutants are adsorbed on the adsorbent surface, and the adsorbent surface plays a key role in this process. Therefore, specific surface area and high porosity are of special importance. The use of nanotechnology and the synthesis of nano adsorbents can increase their performance and efficiency. Nanomembrane plays the role of barrier that separates the two phases by restricting the movement of components in a selective manner. So nanoporous in the membrane can help to reject smaller particle sizes. Nanophotocatalysts, can completely destroy organic pollutants into carbon dioxide and water that are used in the additional treatment stage, and also nanostructures should cause more activate sites for these reactions. As a result, nanotechnology can be a promising solution for having improvement wastewater treatment.

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JOURNAL OF GAS TECHNOLOGY

Volume 7 / Issue 1 / Summer 2022 / Pages 51-60

Journal Homepage: <http://jgt.irangi.org>

Investigation of Water Salinity Effect on Asphaltene Precipitation Using PC-SAFT EOS

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ARTICLE INFO

ORIGINAL RESEARCH ARTICLE

Article History:

Received: 22 April 2022

Revised: 19 May 2022

Accepted: 24 July 2022

Keywords:

Solid model

Asphaltene precipitation

ePC-SAFT EOS

Low-salinity water

Flooding

ABSTRACT

Asphaltene precipitation has attracted more attention in low-salinity water flooding processes in the last decade. In this study, ePC-SAFT equation of state has been used to investigate the effect of water salinity on asphaltene precipitation. To this end, a solid model with a synthetic oil containing heptane and toluene with a ratio of 70 to 30 was used to predict asphaltene precipitation. Three adjustable parameters in the Particle Swarm Optimization method were used to minimize the absolute average deviations (AAD) between experimental and modeling values. The role of water chemistry on asphaltene precipitation was addressed by changing the composition of seawater (SW) by tuning ionic strength and manipulating divalent ions. Also, to get further insights into the role of divalent ions (Mg^{2+} , Ca^{2+} , SO_4^{2-}), three makeup water containing $MgCl_2$, $CaCl_2$ and Na_2SO_4 salts were used. Results showed that in low concentrations of salts (5000 ppm), the asphaltene molecules migrate to the oil/water interface, leading to a decrease in asphaltene precipitation. Beyond this concentration, asphaltene precipitation was increased due to the breaks of the bonding between ion-asphaltene. As to results, a lower precipitation level was observed for the case of dilution seawater (0.5 SW and 0.1SW) that could be discussed in terms of electrical double-layer expansion. The results of the comparison between modeling and experimental data show that the proposed model can predict asphaltene precipitation for $MgCl_2$, $CaCl_2$ and Na_2SO_4 brine with absolute relative deviations less than 7.68%, 5.44% and 8.39%. The finding from this study elucidates the importance of water salinity to design an applicable low-salinity water flooding.

DOR: [20.1001.1/JGT.2022.552432.1000](https://doi.org/10.1001/JGT.2022.552432.1000)**How to cite this article**J. Amanabadi¹, S. Jamshidi², Investigation of Water Salinity Effect on Asphaltene Precipitation Using PC-SAFT EOS. Journal of Gas Technology. 2022; 7(1): 51 -60. (http://jgt.irangi.org/article_698497.html)

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Available online 22 September 2022

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1. Introduction

One of the distinguished methods in enhanced oil recovery (EOR) is low-salinity water flooding (LSWF) which improves oil recovery mostly through wettability alteration, multiple cation exchange, double layer extension, salting-in effect, IFT reduction, etc. (Amanabadi et al., 2020; Chai et al., 2022; Yutkin et al., 2022). Precipitation of asphaltene on the rock surface is one of the unwanted problems during LSWF. This phenomenon could be more challenging if the asphaltene precipitation influences oil recovery by permeability reduction, rock surface wettability alteration, and pipeline blockage (Speight, 2015). Mathematical modeling of this issue has been more attractive to have a better insight into how this phenomenon occurs, prevents, and treats.

The reduction of injected water salinity directly impacts asphaltene presented in the crude oil phase due to their polarity (Hu et al., 2015; Ameri et al., 2018). Hence, several studies have been conducted to address the role of fluid-fluid interaction. To this end, thermodynamic modeling of asphaltene with a different equation of states such as PC-SAFT is essential (Rodriguez, 2008; Sabeti et al., 2015; Meighani et al., 2016). There are two types of asphaltene modeling presented based on the literature. In the first one, it is assumed that asphaltene is an actual component in the oil composition and soluble in the oil. In the second approach, asphaltenes are colloidal in oil, and their stability depends on different factors such as pressure, temperature, and oil composition. Zhang et al. compared PC-SAFT and CPA EOS for the aspect of asphaltene modeling. They used SRK EOS for the physical part, while Wertheim was used for the associating part. They considered asphaltenes as a self-associating component and can cross-associate with resin. They studied six live oils and one heavy oil and found that CPA EOS has better matching with experimental data. The results contradict Alhammadi et al. (Zhang et al., 2012). Kariman Moghaddam and

Jamshidi have suggested a methodology to characterize fluid injections consisting of crude oil and evaluated the performance of the PC-SAFT in asphaltene behavior modeling during fluid injections into the oil reservoirs (Kariman Moghaddam & Jamshidi, 2022). Hosseinifar & Jamshidi modified a new model to estimate PC-SAFT parameters for different pure components. They created a relationship between the cubic equation of state parameters (critical pressure, critical temperature, and acentric factor) and PC-SAFT parameters (Hosseinifar & Jamshidi, 2015). Naseri et al. developed a new multicomponent, multiphase and dynamic tool to model the aggregation and deposition of asphaltene particles in a bulk medium. They developed a bespoke algorithm to predict asphaltene precipitation, aggregation, and deposition. Also, they used PC-SAFT equation of state to obtain asphaltene precipitation phase envelope (APE) (Naseri et al., 2020). Moeini et al. investigated the mechanisms of interfacial tension between oil/ water in the presence of different salt concentrations. Low salinity water flooding (LSWF) causes a reduction of water-oil IFT. They found that interfacial tension reaches its minimum value at a certain salinity which is called critical concentration. Beyond this concentration, diluting brine solution has a negative impact on IFT. The results showed that the amount of IFT decreases until 50% of the brine solution is mixed with deionization water. As soon as brine salinity decreases from critical concentration, the amount of interfacial tension increases (Moeini et al., 2014). Shojaati et al. studied the effect of water salinity on asphaltene behavior in the presence of water in oil emulsion. In order to investigate the effect of ions on the asphaltene instability, makeup waters from different salts were used in a diverse range of concentrations. It was found that divalent cations have more impact on the asphaltene instability compared to monovalent cations due to the chelation process. Furthermore, the presence of divalent anions can prevent the effect of cations on the asphaltene instability (Shojaati et al., 2017). Birkan Demir et al. studied the effect of water

salinity on asphaltene clustering in five different model oils. The brine solutions were prepared with various salts, including CaCl_2 and MgCl_2 at 2%, 4%, 6%, and 8% concentrations. The results showed that the makeup water with CaCl_2 salt results in bigger asphaltenes clusters than NaCl salt (Birkan Demir et al., 2016).

In our previous study, the mechanisms between rock/fluid in the presence of different water salinity was examined (Amanabadi et al., 2021). As to the literature on asphaltene precipitation for the purpose of LSWF, comparatively, few studies addressed modeling of asphaltene precipitation in the presence of makeup water compositions and model oil. In order to understand the exact mechanism behind the asphaltene precipitation, makeup water, including single salts (such as MgCl_2 and CaCl_2) in different ionic strengths, is used. Also, formation water and seawater have been used to simulate reservoir conditions better.

2. Material and Methods

2.1. ePC-SAFT

In this study, the ePC-SAFT EOS proposed by Cameretti et al. was used to model the electrolyte solutions (Cameretti et al., 2005). As offered by Gross et al., the original PC-SAFT was used to model the other components such as hydrocarbons and water (Gross et al., 2001).

$$\frac{A^{res}}{NKT} = a^{res} = a^{hc} + a^{disp} + a^{assoc} + a^{ion} \quad (1)$$

Where N is the total number of molecules, a^{hc} is the residual Helmholtz energy of hard-chain, a^{disp} , a^{assoc} and a^{ion} are Helmholtz energy for dispersive, associative, and ions, respectively. Finally, the Helmholtz energy of ions is defined as follows:

$$\frac{a^{ion}}{K_B T} = -\frac{\kappa}{12\pi K_B T \epsilon} \times \sum_j x_j q_j^2 X_j \quad (2)$$

Where K_B is Boltzman constant, x_j and q_j are the mole fraction and charge of ions, respectively. Finally, X_j and inverse of Deby length (κ) are defined as follows:

$$X_j = \frac{3}{(\kappa a_j)^3} \times \left[\frac{3}{2} + \ln(1 + \kappa a_j) - 2(1 + \kappa a_j) + \frac{1}{2}(1 + \kappa a_j)^2 \right] \quad (3)$$

$$\kappa = \sqrt{\frac{N_A}{K_B \epsilon} \times \sum_j q_j^2 c_j} = \sqrt{\frac{\rho_N e^2}{K_B T \epsilon} \sum_j Z_j^2 x_j} \quad (4)$$

Where N_A is Avogadro's constant, e is the elementary charge (c), and c_j molarity (mol/lit)

2.2. Calculation of thermodynamic properties with ePC-SAFT

In this study, to calculate the compressibility factor from residual Helmholtz energy, the following equation was used:

$$Z = \frac{\partial(a)}{\partial \ln(\eta)} = \eta \frac{\partial a}{\partial \eta} \quad \text{or} \quad Z = \frac{\partial a}{\partial \ln(\rho)} = \rho \frac{\partial a}{\partial \rho} \quad (5)$$

Where a is the total contribution of Helmholtz energy including a^{hc} , a^{disp} , and a^{assoc} , and η is residual density. Other residual Helmholtz energy is defined as follows:

$$\tilde{a}^{hc} = \bar{m} \tilde{a}^{hs} + \tilde{a}^{chain} = \bar{m} \tilde{a}^{hs} + \sum_i x_i (1 - m_i) \ln g_{ii}^{hs}(d_i) \quad (6)$$

$$\tilde{a}^{hs} = \frac{1}{\zeta_0} \left(\frac{3\zeta_1 \zeta_2}{1 - \zeta_3} + \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3} - \zeta_0 \right) \ln(1 - \zeta_3) \right) \quad (7)$$

$$\tilde{a}^{disp} = \frac{a^{disp}}{RT} = \frac{A_1}{RT} + \frac{A_2}{RT} \quad (8)$$

$$\frac{A_1}{NKT} = -2\pi\rho N_A \left[\sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{KT} \right) \sigma_{ij}^3 \right] \int_1^\infty \bar{u}(x) g^{hc}(m; \bar{x} \frac{\sigma}{d}) x^2 dx \quad (9)$$

$$\frac{A_2}{NKT} = -\pi\rho N_A \bar{m} C_1 \left[\sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{KT} \right)^2 \sigma_{ij}^3 \right] \int_1^\infty \bar{u}(x)^2 g^{hc}(m; \bar{x} \frac{\sigma}{d}) x^2 dx \quad (10)$$

Where a^{hs} is Helmholtz energy of the hard-sphere, m_i is the number of the segment that is equal to 1 for ions, $g_{ij}^{hs}(d_i)$ is the radial distribution function, ϵ_{ij}/KB is the pairing segment energy parameter, A_1 and A_2 are depend on density, compositions, and size of molecules. The liquid-liquid flash calculation for oil/water was used to find the fugacity of precipitated asphaltene in the liquid phase (at atmospheric pressure and 353.15 k).

$$f_i^h = f_i^w \quad (11)$$

$$\phi_{i,p} = \exp \left(\frac{a_p^{res}}{RT} + (Z_p - 1) + \frac{\partial(a_p^{res}/RT)}{\partial x_i} - \ln(Z_p) - \sum_{j=1}^N x_j \left(\frac{\partial(a_p^{res}/RT)}{\partial x_i} \right)_{T,Y,x_{i \neq j}} \right) \quad (12)$$

Where $\phi_{i,p}$ is the fugacity coefficient of phase p .

2.3. Nghiem model

In this study, the Nghiem model (Nghiem et al., 2000) was used to predict asphaltene precipitation in the presence of water salinity. This model relies on the fugacity coefficient compared to other thermodynamic models (colloidal, activity coefficient base model). Also, the fugacity of asphaltene is expressed as a pure solid phase as follows:

$$\ln f_s = \ln f_s^* + \frac{v_s(P - P^*)}{RT} \quad (13)$$

Where f_s is the fugacity of asphaltene, f_s^* is the fugacity of asphaltene at a reference pressure, P^* , T , and R are reference pressure, temperature,

and the universal gas constant, respectively.

Three adjustable parameters in the Particle Swarm Optimization algorithm that was implemented in the Csharp language were used to minimize the AAD percentage between experimental and modeling data. Asphaltene's fugacity in the pure solid, interaction between asphaltene and ions, and interaction of asphaltene with water are considered as adjustable parameters where the objective function is defined as follows:

$$AAD\% = 100 \frac{\sum_{i=1}^N (abs(Prec\%_{exp,i} - Prec\%_{model,i}) / Prec\%_{exp,i})}{N} \quad (14)$$

Where $Prec\%_{exp,i}$ is asphaltene percentage of asphaltene precipitate obtained from experimental data, $Prec\%_{model,i}$ is the amount of asphaltene precipitate from the model, and N is the number of experimental data. The schematic of asphaltene precipitation calculation with respect to Nghiem model is shown below.

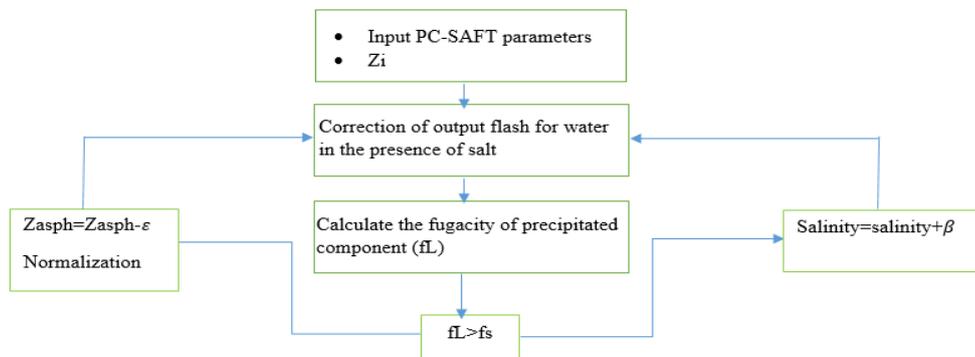


Figure 1. The schematic of asphaltene precipitation calculation

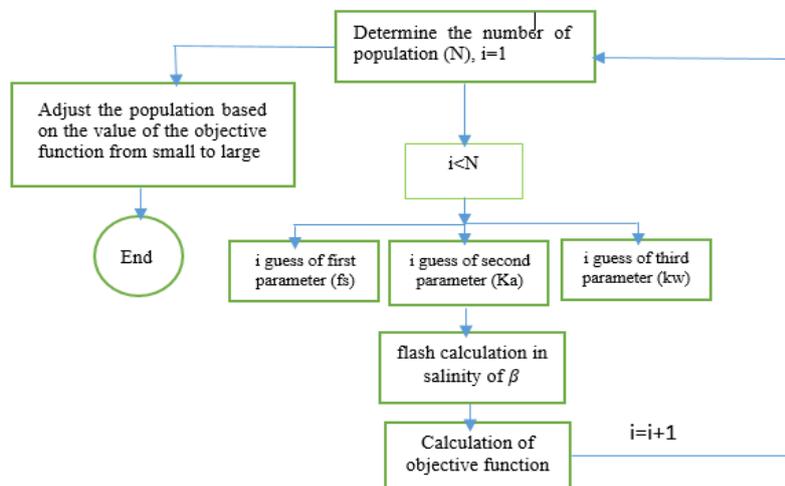


Figure 2. The procedure of optimizing adjustable parameter

2.4. Fluids

In this study, to check the effect of divalent ions on the asphaltene precipitation, three types of makeup water were used that in each solution, only one of the divalent salts became present. Also, to check the effect of seawater and

formation water on asphaltene precipitation, two solutions, including different salts, were used. Furthermore, in order to check the impact of salinity, two (0.5SW) and ten (0.1SW) time dilutions of seawater were used. See Table 1.

Table 1. Composition of seawater and formation water (Hosseini, 2018)

Brine: Formation water		Brine: Seawater			
Salt	Amount (gr/L)	Salt	SW (gr/lit)	0.5SW (gr/lit)	0.1SW (gr/lit)
NaCl	137.2735	NaCl	1.4212	0.71	0.1421
KCl	0	KCl	0.04125	0.02	0.0041
CaCO ₃	1.6278	MgCl ₂	0.3215	0.16075	0.0321
MgCl ₂	53.37	CaCl ₂	0.0692	0.045	0.0069
CaCl ₂	6.098	Na ₂ SO ₄	0.2245	0.1121	0.0224
Na ₂ SO ₄	2.587	NaHCO ₃	0.0053	0.0042	0.005
NaHCO ₃	2.587				
TDS (gr/50cc)	9.4844	TDS(gr/50cc)	2.08	1.04171	0.208

2.5. Oil

Due to the complex structure of crude oils, the observed changes in interfacial tension and asphaltene precipitation cannot be accurately attributed to the effect of a particular component. In such cases, the model oil can be used to facilitate the study of mechanisms. It is easier to interpret the observed phenomena when model oil is used because only one parameter is considered to change in the model oil. To this end, model oil containing heptane and toluene in a ratio of 70 to 30 was used to examine the effect of water salinity on asphaltene precipitation. The density of model oil is 0.84 (gr/m³), and asphaltene was measured as 0.6 of its total weight percent. Also, to prepare the input data for makeup water, a specific amount of salts (1000, 5000, 15000, 30000 and 45000 ppm) was added to the water (Hosseini, 2018).

3. Results and discussion

In general, it is necessary to pay attention to the reactions between water and salts in aqueous solutions, while it produces new ions in water. These ions migrate to the contact surface of water and oil. As a result, interactions between asphaltene and ions lead to a change in surface tension and consequently in the final amount of asphaltene precipitation.

Figure 3 shows the effect of makeup water in MgCl₂ salt on asphaltene precipitation. Based on the result, asphaltene precipitation decreased with increasing concentration up to 5000 ppm at low concentrations. Beyond this concentration, increases in salt concentration lead to increases in the amount of asphaltene precipitation that can be explained by the concept of salting-in and salting-out effect. Asphaltene molecules in the oil phase can play the role of polydentate ligand in the presence of cations. According to the definition, ligands are molecules or atoms with a

lone pair of electrons that can have neutral and negative electron charges in the external layer. Therefore, ligands usually interact with metal ions and make a complex structure. Generally, the relationship between metal and ligand involves one or more pairs of ligand electrons. In other words, at low salinities, the mobility of asphaltene molecules towards the interface of water and oil increases due to the presence of ions in the aqueous phase. Among these ions, cations play an essential role in binding to the structure of ligands (asphaltenes). Therefore, at low salinities, the asphaltene separates from the resins surrounding them and moves toward the interface. The Brownian motion of the asphaltene molecules toward the interface causes them to collide and makes their aggregation possible. On the other hand, due to the negative charge in the external structure of asphaltene, they have a function similar to surfactants and communicate with water molecules at the interface, the interaction between water-ion and water-asphaltene in the interface leading to a decrease in interfacial tension that could be proven by measuring interfacial tension by Hosseini et al. Beyond 5000 ppm, with increasing the ionic strength of aqueous phase relative to the interface, the thermodynamic equilibrium of the system is disturbed leading to increased demand of ions for ionization. Eventually, the bonding created at the interface is broken, and a layer of asphaltene with Brownian motion returns to the oil phase leading to the aggregation and precipitation of asphaltene. Also, the results obtained from the model were validated by the experimental data in Hosseini, 2018.

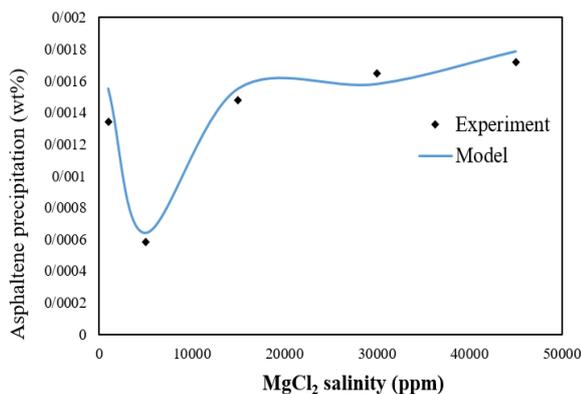


Figure 3. The effect of makeup water with MgCl₂ salt on asphaltene precipitation

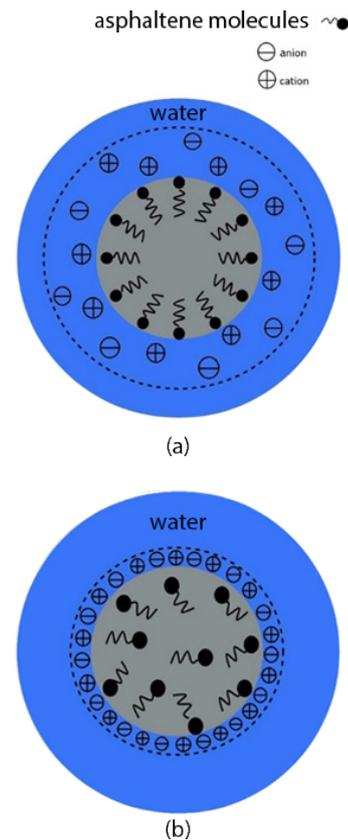


Figure 4. The effect of salinity on electrical double layer expansion. a) low salinity b) high salinity

Figure 5 shows the effect of makeup water in CaCl₂ salt on asphaltene precipitation. The mechanism of asphaltene precipitation in the presence of CaCl₂ salt is similar to MgCl₂, but the reason for the difference between the two trends could be discussed in terms of activity coefficient. The activity coefficient of each salt is unique for any particular concentration. Furthermore, the degree of ions hydration considered in terms of dispersive energy is different at any ionic strength of the solution leading to attract water molecules located in the interface toward the bulk phase of water. This attraction increases as the ratio of cation charge to cation surface increases. According to the results, in low concentrations of CaCl₂ (1000 and 5000 ppm), the asphaltene molecules are ionized by Ca²⁺ cations leading to the migration of asphaltene molecules toward to interface. Asphaltene molecules behave as a surfactant and reduce the interfacial tension. Beyond this concentration, increasing the

salinity, the electrical double layer becomes very thin, leading to the negative surface excess asphaltene concentration, which ultimately increases precipitation. In high concentrations, with a close look at the asphaltene precipitation diagram versus $MgCl_2$ and $CaCl_2$ concentration, understand that the rate of increase in precipitation is higher for $MgCl_2$ than $CaCl_2$ because the ratio of cation charge to cation surface is higher for Mg^{2+} than Ca^{2+} leading to a higher amount of hydration in the aqueous phase. The obtained results indicate that the model is in good agreement with experimental data. Also, the results obtained from the model were validated by the experimental data in Hosseini, 2018.

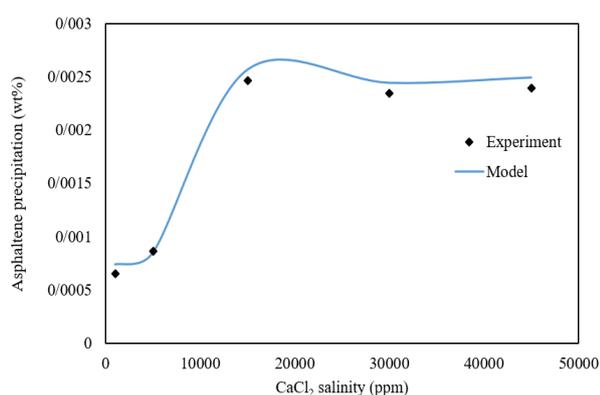


Figure 5. The effect of makeup water with $CaCl_2$ salt on asphaltene precipitation

Figure 6 shows the effect of makeup water in Na_2SO_4 salt on asphaltene precipitation. In order to investigate the effect of salinity on asphaltene precipitation, five brine solutions with Na_2SO_4 were used in different concentrations (1000, 5000, 15000, 30000, 45000 ppm). The result screens out, from the salinity of 1000 ppm to 5000 ppm, asphaltene precipitation decreases due to ionization of asphaltene molecules and their migration toward the interface. Beyond this point, the asphaltene precipitating was reduced by salting-out effect mechanism with a further increase in salinity. Generally, it has been proven 2:1 electrolyte (divalent cation in the presence of monovalent anion) like $MgCl_2$ and $CaCl_2$ have a higher activity coefficient than 1:2

electrolytes (divalent anions in the presence of monovalent cations) like Na_2SO_4 , which can be related to the higher electron density of divalent cations than divalent anions. Also, the dispersive energy parameter confirms mentioned logic (Mg^{2+} and Ca^{2+} have a higher value than SO_4^{2-}). Consequently, Na_2SO_4 salt has less ability to ionize asphaltene toward the interface. Thus, IFT changes are less than in previous cases. However, in low salinities, the amount of asphaltene precipitation decreases due to the presence of asphaltene in the interface. Also, as mentioned before, according to the salting-out effect, asphaltene precipitating was reduced due to an increase in salinity. The obtained results indicate that the model is in good agreement with experimental data. Also, the results obtained from the model were validated by the experimental data in Hosseini, 2018.

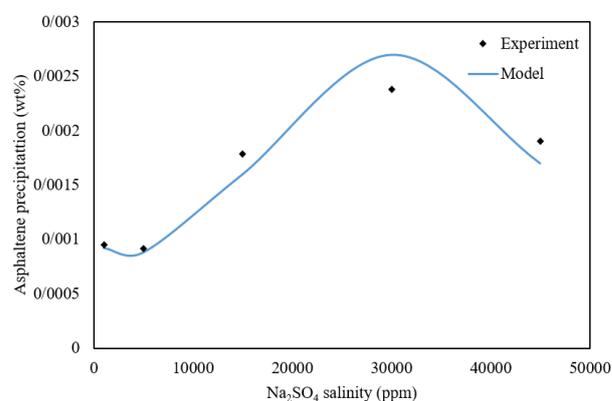


Figure 6. The effect of makeup water with Na_2SO_4 salt on asphaltene precipitation

In the previous three sections, the impact of monovalent and divalent salt on asphaltene precipitation was observed. But in reality, the water that exists in the reservoir is a combination of different salts with different impacts on the precipitation mechanism. To this end, modeling of asphaltene precipitation in the presence of seawater and formation water was conducted.

Figure 7 shows the impact of formation water and Persian Gulf seawater salinity in different dilutions of salts on asphaltene precipitation. The compositions of salts are given in Table 1. Based on the results, in the formation water,

due to the presence of different concentrations of ions, the ionic strength of water increased, leading to a decrease in Deby length. The water molecules return to the aqueous phase to hydrate more ions. Afterward, asphaltene molecules immigrate to the oil phase, which causes precipitation. Also, from formation water to ten times seawater dilution, the asphaltene precipitation decreases due to an increase in Deby length, which causes a regular arrangement of asphaltene in the interface. However, many articles studied the nonmonotonic behavior of interfacial tension versus salinity. But it is necessary to mention that the oil that has been used in this study consist of heptane and toluene and does not contain acidic components such as naphthenic acid. The competition between asphaltene molecules and naphthenic acid makes optimum conditions for IFT. Also, the results obtained from the model were validated by the experimental data in Hosseini, 2018 and Shojaati et al., 2017.

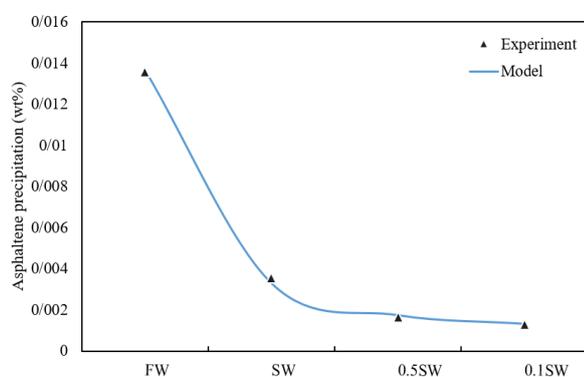


Figure 7. The effect of salinity on asphaltene precipitation in the presence of formation water (FW), Persian Gulf seawater (SW), two times dilution of seawater (0.5SW), and ten times dilution of seawater (0.1SW)

4. Conclusion

In this paper, ePC-SAFT equation of state was applied to many electrolyte systems. The aim of this work was modeling of asphaltene precipitation in the presence of different brines such as makeup water with $MgCl_2$, $CaCl_2$, and Na_2SO_4 , salts, formation water, and seawater with different dilutions (two and ten times

diluted), Also, to get a better understanding from the mechanisms during precipitation, model oil containing heptane-toluene was used. Results of the comparison showed that the proposed model is capable of predicting asphaltene precipitation for $MgCl_2$, $CaCl_2$ and Na_2SO_4 , brine with absolute relative deviations less than 7.68%, 5.44% and 8.39%, respectively. At low concentrations, the salting-in effect mechanism was observed due to the ionization of asphaltene molecules toward the oil-water interface. Also, asphaltene molecules act as a surfactant and bond with water molecules in the interface leading to a decrease in precipitation. Furthermore, in high salinity, the water molecules cannot support the bonding between ion and asphaltene due to the thin electrical double layer. It breaks down and leads to the return of asphaltene molecules to the oil phase. Eventually, the Brownian motion of asphaltene molecules in the oil phase and collisions lead to aggregation and precipitation. Furthermore, due to the presence of different ions, in the formation water and seawater, the ionic strength is high, and the electrical double layer is very thin, causing the further hydration of cations in the aqueous phase.

Nomenclature

a	Reduced Helmholtz free energy
d	Temperature-dependent segment diameter
D	\AA^0
$g^{hs}(r)$	Diffusion Coefficient
\bar{m}	Radial distribution function for hard-sphere
N	sphere
N_{av}	mean segment number in the system
fL	Total number of molecules in the system
	Avogadro's number
Z_i	Fugacity of precipitating component in the hydrocarbon phase
P	hydrocarbon phase
q_j	Charge number
T	Pressure (pa)
x	Charge of ion j (C)
	Temperature (k)
	Mole fraction

Greek letters

$\frac{\varepsilon}{k_B}$	Pure component segment energy parameter
$\frac{\varepsilon_{ij}}{k_B}$	Pair segment energy parameter
ζ_k	Density function (for $k = 0:3$)
$\eta(=\zeta_3)$	Reduced density
π	Irrational number (3.14159265)
ρ	Molar density ($\frac{mol}{A^3}$)
σ	Temperature independent segment diameter
Ψ	Electron potential
ε	Dielectric constant of a medium, $\varepsilon_r \varepsilon_0 (\frac{C}{Vm})$
\emptyset	Fugacity coefficient

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Material Selection Strategy for Corrosion Control in Iranian Upstream Oil and Gas Industry

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ARTICLE INFO

REVIEW ARTICLE

Article History:

Received: 29 June 2022

Revised: 17 August 2022

Accepted: 24 August 2022

Keywords:

Material selection

Corrosion

Oil and Gas industry

Corrosion management

ABSTRACT

Annually, a huge amount of money is lost due to corrosion problems in upstream and downstream oil and gas industries. To control the corrosion costs, recently, corrosion control/corrosion management concept is developed. The aim of corrosion management philosophy is to reduce corrosion costs and increase safety by re-evaluation process in different stages of the project. The material selection process is one of the key stages in integration assurance of the system, which plays important role in the overall corrosion control process. Some important parameters in selecting suitable materials for use in a given working and environmental condition includes design pressure and temperature, weldability, costs and corrosion concerns. Nowadays, the last one attracted the attention of the both researchers and owners. Codes like ISO 21457 necessitate providing Material Selection Procedure Report before proceeding executive steps of the project. Without any specific material selection procedure; the material selection process will be a complex and confusing task because of the diversity in codes and fluid service conditions. This study aims to introduce researchers and engineering with corrosion concerns especially in CO₂, H₂S, and salt contained services and the solutions which are normally employed in the upstream oil industry to deal with associated problems. Towards, environmental deterioration problems the oil and gas fields of Iran are discussed and the related treatments are presented.

DOR: [20.1001.1/JGT.2022.559752.1002](https://doi.org/10.1001.1/JGT.2022.559752.1002)

How to cite this article

M. Eskandarzade, A.Kalaki, M. Safajou-Jahankhanemlou, M. Najafi Ershadi, Material Selection Strategy for Corrosion Control in Iranian Upstream Oil and Gas Industry. Journal of Gas Technology. 2022; 7(1): 61 -69. (http://jgt.irangi.org/article_699817.html)

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Available online 22 September 2022

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1. Introduction

Pipes, fitting, valves, and the other products which are used in oil and gas well-head and production lines shall be selected in a way that withstands internal pressures due to service fluids, besides the external loads by bending, tension and/or temperature expansion/contraction. ASME SEC VIII describes the rules for construction of the pressurized products (ASME BPVC, 1998). In addition to mechanical strength evaluation, these products should assure the integrity of the system for the whole design life. It means that they should be selected enough strong to eliminate corrosion attacks by the environmental conditions and to resist the internal and external corrosive environment. The importance of corrosion control in oil and gas industry is very clear and many studies dedicate to investigating different aspects of corrosion phenomena in energy transportation systems via pipes (Eskandarzade et al., 2018). There are plenty of steel materials with different corrosion resistance characteristics. The material composition and even the fabrication method of the product are very important in corrosion rate during the service. The effects of Chromium on corrosion behavior of Low-alloy Steel has been studied by Zhou et al. (2015). According to their report, the increase of chromium content results in the improvement of corrosion resistance of the Low-alloy Steel. The assessment of localized corrosion in carbon steel is reported by Nasirpour et al. (2014). Effects of chloride content on CO₂ corrosion of the carbon steel in simulated oil and gas well environments are investigated by Liu et al. (2014).

Several researchers who have used theoretical models to investigate the effects of influencing parameters in the integrity of the pipeline/piping systems. Shabarchin and Tesfamariam (2017) have assessed the risk of seismicity and the internal corrosion on the oil and gas pipeline infrastructure. Zhou et al. (2016) have tried to estimate the probability of the corrosion failure in petroleum industry

using the fuzzy logic method.

Choosing among materials to manage the corrosion rate needs a very careful understanding of the working conditions especially the severity of the service fluid. In Iran to calculate the severity of the service fluid, Drill Stem Test (DST) (Bredehoeft, 1965) is normally used to identify the fluid composition of the reservoir. The result of these tests usually lists the H₂O, CO₂, salt, and other fluid content of the crude oil or gas.

In addition to the fluid service severity, other criteria such as the safety and easy-to-repair level should be considered in the material selection process. As a rule of thumb, it should be taken extra attentions to products that are used in hard-to-repair locations.

Corrosion management in oil and gas industry is a continuous process from design and construction to operations (Dawson, 2010). It is also a team effort that involves a range of expertise from corrosion engineers, materials specialists, reservoir engineers, and process engineers. This study concentrated on the corrosion measures which are taken in Iranian Oil and Gas fields during material selection process. These measures are normally taken based on the international codes as well as the long-term experience of the Iranian National Oil Company. The focus of this study is on low carbon steel alloys and their internal corrosion problems. Towards, the most frequent aggressive environments in Iranian Oil and Gas wells; such as H₂S, CO₂, chloride contents and their corrosion mechanisms will be discussed and the related treatments will be described.

2. Corrosion Study

Corrosion study is an inevitable part of the material selection process. It usually considers both erosion and corrosion mechanisms. Production of sand and other solids are common in the most of oil and gas wells. Therefore, the presence of the simultaneous erosion and corrosion mechanisms during the service life is very common. The aim of corrosion study is to

find that how much the fluid in service is corrosive and aggressive to the materials. Corrosion evaluations and calculations can be based on the well-known corrosion models (such as Sell model, Norsok) (Olsen, 2003), laboratory tests or field experiences. Using last method requires the well-documented successful experience of the material usage at the specific service fluid condition for at least two years. According to NACE MR0175, if it is the case, the usage of the same material at the similar service condition is acceptable. Most of the crude oil and gas production lines in Iran can be categorized as wet hydrocarbons. For this type of fluid services the possible corrosion mechanisms for carbon steels are listed in Table 1 which should be considered in corrosion evaluations. To do so, firstly the composition of the production fluid should be understood. Table 3 indicates a typical composition of the production fluid in Central Oil Fields of Iran.

Table 2 has been obtained from DST results. Normally, fluid samples, reservoir pressure, formation properties, productivity estimates including flow rate and hydrodynamic information are the data can be obtained from a DST. According to the results from this test, the oil and gas fields can be categorized as sour or sweet services. In next sections corrosive compounds in oil and gas fields are described and the fundamental for material selection in Iranian Companies are presented.

Table 1. Corrosion Mechanisms which are possible in Oil and Gas industry

Corrosion Mechanism	Corrosion Mechanism (Continue)
General Corrosion due to CO ₂ & H ₂ S	Pitting
SSC/SCC caused by H ₂ S	Dissolved Oxygen corrosion
HIC/SWC	ASCC
MIC	

3. H₂S Corrosion

3.1. Wet-H₂S Content Fluids

If the water exists at the service fluid, then the

H₂S damage can be observed at the carbon steel; but the dry H₂S is not deteriorative. In general, the damage rate of the wet-H₂S is depending on the amount of liquid water and the partial pressure (PP) of the H₂S. Since, the partial pressure of the H₂S is directly related to the total pressure of the fluid (Eq. 1); then, it can be concluded that as the working pressure increases, the corrosion rate due to the H₂S increases, dependently.

$$P_{H_2S} = P_{total} \text{ Mole\% } H_2S \quad (1)$$

Other important factors in corrosion rate of the H₂S compound are including: in situ pH, H₂S level, contaminants, temperature. Standard NACE MR0175-P2 has categorized H₂S content fluids into four regions including Region zero (sweet service), Region 1 (Mild sour service), Region 2 (Medium sour service) and Region 3 (severe sour service) based on in situ pH and H₂S partial pressure (Figure 1).

Table 2. Typical reservoir fluid composition for a gas well located in Iranian Central Gas Fields

Component	Partial Pressure (Bar)
H ₂ S	4.34
CO ₂	5.40
N ₂	26
C ₁	127
C ₂	8.40
C ₃	3.47
ISO-C ₄	0.78
N-C ₄	1.50
ISO-C ₅	0.70
N-C ₅	0.62
C ₆	1.05
C ₇₊	3.44
Total	100
C₇₊ Properties	
Specific gravity	0.76
Molecular weight	121.02
Fluid Properties	
API	
TEMP (°F)	170
GOR (SCF/STB)	29.82

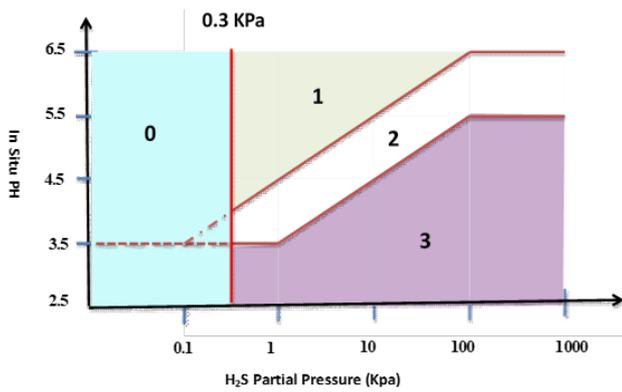


Figure 1. H₂S environment severity for SSC cracking in carbon steels (NACE MR0175, 2001)

3.2. Wet-H₂S Induced Damages

The deterioration of metal due to contact with hydrogen sulfide (H₂S) is called sour corrosion. Hydrogen sulfide when dissolved in water produces a weak acid, its general corrosion is rare a problem (Kane and Cayard, 1999); but it is the source of atomic hydrogen and known to be the main reason for the occurrence of the several types of cracks. Major defects induced by hydrogen sulfide are illustrated in (Figure 2). Among all defects, SSC is the most crucial crack type. SSC is the combined influence of hydrogen sulfide and tensile stress. It propagates over the ranges of velocities from 10⁻³ to 10mm/h depending upon combination of alloy and the environment involved (Popoola, 2013). Then, this type of crack can grow very fast and catastrophic failure can occur in hours/days. SSC is also less likely to be founded during the periodic inspections.

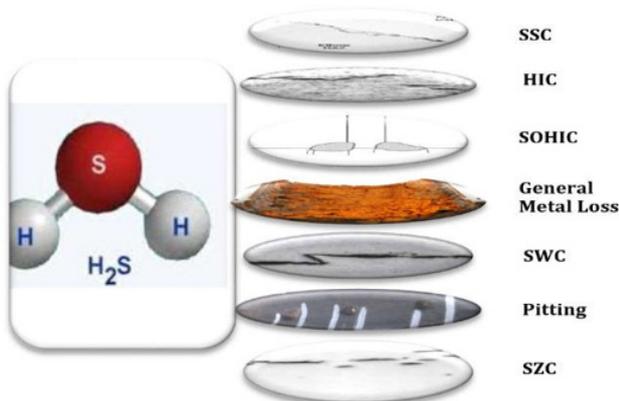


Figure 2. The hydrogen sulfide induced major defects

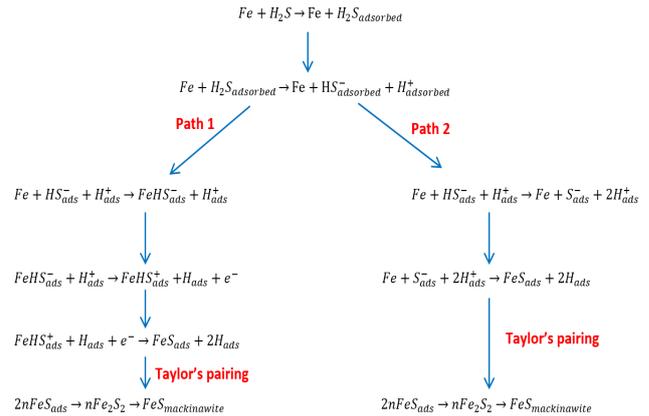


Figure 3. The Proposed mechanism for H₂S corrosion on steel (Koteswaran, 2010)

For this reason, where the SSC is the probable defect type; choosing SSC resistance materials is priority in the material selection process.

3.3. Mechanism of H₂S- Induced Defects

The internal corrosion of carbon steel in the presence of hydrogen sulfide represents a significant problem for both oil refineries and natural gas treatment facilities. Surface scale formation is one of the important factors governing the corrosion rate. The scale growth depends primarily on the kinetics of scale formation. In contrast to relatively straightforward iron carbonate precipitation in pure CO₂ corrosion, in an H₂S environment many types of iron sulfide may form such as amorphous ferrous sulfide, mackinawite, cubic ferrous sulfide, smythite, greigte, pyrrhotite, troilite and pyrite, among which mackinawite is considered to form first on the steel surface by a direct surface reaction (Sun and Nestic, 2007). The poorly known mechanism of H₂S corrosion makes it difficult to quantify the kinetics of iron sulfide scale formation. A probable mechanism for Iron dissolution in aqueous solutions containing H₂S based on the formation of mackinawite film, as proposed by Sun et al (2008) is shown in (Figure 3).

4. CO₂ Content Fluids

Similar to H₂S, CO₂ can lead to metal corrosion just at the presence of the liquid water. The comprehensive study of the CO₂ corrosion has been done by the European Federation of Corrosion (EFC)

and reported as EFC-23. It causes both general and localized corrosion types. Steels are very unstable when exposed to dissolved CO₂ in water; but after a first layer corrosion, stable protective scale of FeCO₂ is produced which hinders the corrosion of internal layers of the metal.

4.1. CO₂ Induced Corrosions (Sweet Corrosion)

CO₂ related problems are widely described in publication of European Federation of corrosion (Kermani and Smith, 1997). Major corrosion types due to CO₂ are illustrated in (Figure 4).

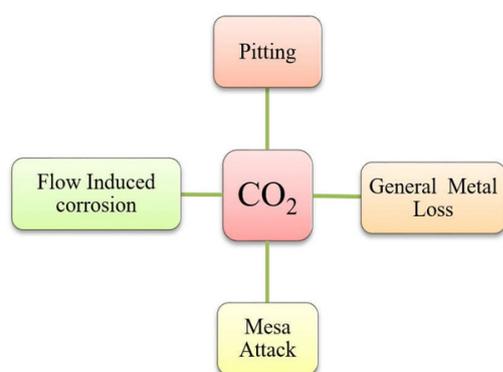


Figure 4. Major corrosion mechanisms due to CO₂

General Corrosion: Dissolved CO₂ in water reacts with metal and produces Iron Carbonates. This type of corrosion is one of the most critical considerations in calculation of Corrosion Allowances.

Pitting: In low speed flows this type of corrosion can occur in any temperature. However, the rate of pitting increases by increasing temperature and the partial pressure of the CO₂. Depending on chemical composition of the material, there is a given temperature which the rate of the pitting is highest in this temperature; for carbon steels used in oil and gas industry the range of critical temperature is 80-90 Celsius.

Mesa attack: Mesa is the name of a mountain in USA and also the special type of pitting is named Mesa because of the shape similarity of this type of pitting with Mesa Mountain. In a special condition (flow speed: 0.1-7 m/sec; temperature: 40-80 degrees; partial pressure of CO₂ greater than 1.5 bars) the Iron Carbonate

scale can be removed due to the contact of solids and the produced locally bare steel surface is corroded and this phenomenon is repeated until the localized Mesa attack with flat bottom and clear edges occurred.

Flow induced localized corrosion: This type of corrosion is the result of removing of protective scale in a region of previously produced localized corrosions. Hence, a bigger area of the metal is exposed to corrosion.

Most influencing parameters in CO₂ corrosion are including water-cut, water analysis, fugacity of CO₂. Fugacity of CO₂ is influenced by total pressure and temperature and can be found from Table 2.B13.2 of standard API-RP580 (2016). Also, the calculating of CO₂ corrosion rate can be done using the relations offered in this standard (Eq. 2):

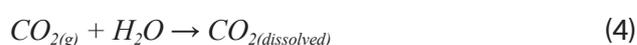
$$CR_{base} = f(T, pH) \cdot f_{CO_2}^{0.62} \cdot \left(\frac{S}{19}\right)^{0.146+0.0324 f_{CO_2}} \quad (2)$$

In this equation f is the fugacity; S is the shear stress of the fluid. The shear stress of the fluid is calculated as following [18]:

$$S = \frac{f \cdot \rho_m \cdot u_m^2}{2} \quad (3)$$

4.2. Mechanism of CO₂ induced defects

Dissolved CO₂ in water produces carbonic acid which is rich in atomic hydrogen. The most common chemical reactions which are common at the presence of CO₂ and H₂O follows (Kermani and Smith, 1997):



However, the actual mechanisms of a localized corrosion of carbon steels in CO₂ environments are not clear, and there are no rules for its prediction. As discussed before a produced iron carbonate is very protective scale; when this protective scale is locally damaged due to contact of solid particles or the flow of the fluid; the chloride salts can touch the uncoated surface of the steel and the iron

chloride is replaced with iron oxide in these regions. As the mole volume of the iron chloride is greater than the mole volume of the iron oxide; it causes the break of more protective iron carbonate scale and the corrosion extended (Davies and Burstein, 1980). Bare areas act as an anode of a galvanic cell where surrounding film-covered areas operate as the cathode. It is assumed that the repetition of this procedure constitutes the localized corrosion mechanism at the presence of wet- CO_2 .

5. Combined CO_2 and H_2S Content Fluids

Corrosion mechanism and the H_2S induced cracks changes by changing in pH level of the fluid. The presence of both CO_2 and H_2S cause the reduction in pH level of the fluid and hence, increase the severity of the corrosive environment and consequently the occurrence of the crack and the other defects. The value of in situ pH can be obtained using Figure 5. It should be noted that if the fluid is containing bicarbonate ions or other influencing elements, then Figure 5 is not valid and other suitable curves should be employed. The presence of a small concentrations of H_2S can have a significant effect on the CO_2 corrosion; this is because iron sulfide can precipitate as the corrosion product in $\text{CO}_2/\text{H}_2\text{S}$ environments. Depending on the exposure conditions, different forms of FeS can form and their specific corrosion protectiveness may be different. There

are currently no generally accepted predictive algorithms for any form of H_2S corrosion. There are also still several unknowns about the corrosion reactions that lead to pitting, which is the most common mode of sour service equipment failure. To determine how much H_2S is required to turn a system from sweet to sour corrosion, different rules of thumb have been used. In the 1980s, Dunlop et al. proposed the use of a $\text{CO}_2/\text{H}_2\text{S}$ ratio of 500 at 25°C to determine whether the corrosion product will be FeCO_3 or FeS . For values greater than 500, the product will be FeCO_3 and for values less than 500 the product will be FeS . Other authors proposed a ratio of $\text{CO}_2/\text{H}_2\text{S}$ lower than 20 to have sour corrosion, while a mixed regime is considered when the ratio ranges between 20 and 500 and sweet corrosion for values higher than 500.

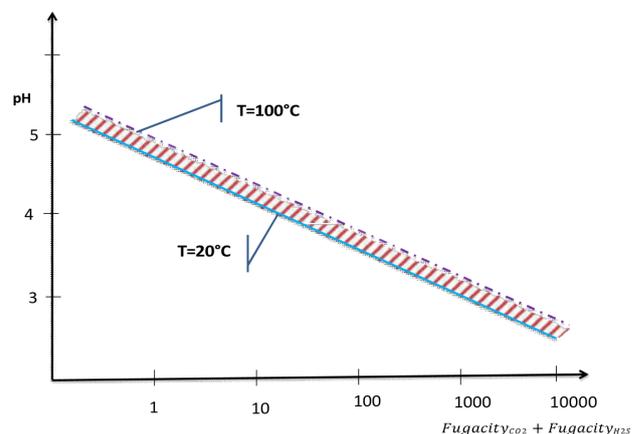


Figure 5. In situ pH of the condensed water under the CO_2 and H_2S pressure (NACE MR0175, 2001)

Table 3. Material Selection Rules for Different Fluid Condition

Corrosive Media	Possible Failure Type	Actions
H_2S (Partial pressure lower than 0.05 bar)	General Corrosion	Generally, no action needed for H_2S content, however, the following should be noted: <ul style="list-style-type: none"> – Design should be based on other corrosive element types. – Avoid using materials susceptible for SSC and HSC. – Avoid using steels with yield strength greater than 965 MPa; if is inevitable, SSC and HSC tests are required. – Extra attention should be made for crack possibility in high concentrated load points.
H_2S (Partial pressure greater than 0.05 bar)	SSC, Pitting, HIC, SOHIC, SWC, SZC, General corrosion.	<ul style="list-style-type: none"> – Selection of material based on Appendix A of Standard NACE MR0175 P2 or using other methods of material selections in this standard. – Hardness in welding zone should be controlled according to NACE MR0175 P2; Table A.1. In general, the hardness of the heat affected zone and other sections should not be greater than 22 RC; otherwise Post Weld Heat Treatment is required.
CO_2 partial pressure less than 0.5 bar (Low risk)	General corrosion	No special action is needed

Table 3. Material Selection Rules for Different Fluid Condition (Cont'd)

Corrosive Media	Possible Failure Type	Actions
CO ₂ partial pressure in the range of 0.5 to 2 bars (Medium risk)	General corrosion	<ul style="list-style-type: none"> - Higher Corrosion allowance should be considered. - Maximum weld metal penetration should be 0.5mm. - It is recommended using copper content filler metals for root welding (e.g. AWS-7018-G) - Using of suitable inhibitors
CO ₂ partial pressure greater than 2 bar (High Risk)	General Corrosion, Pitting, Mesa attack, flow induced attack.	<ul style="list-style-type: none"> - Corrosion Resistant Alloys should be used - Maximum weld metal penetration should be 0.5mm. - It is recommended using copper content filler metals for root welding (e.g. AWS-7018-G) - Using of suitable inhibitors
Combined H ₂ S and CO ₂ (CO ₂ /H ₂ S<20)	Depends on H ₂ S partial pressure	<ul style="list-style-type: none"> - Related H₂S partial pressure measures should be considered. - Related CO₂ partial pressure measures should be considered
Combined H ₂ S and CO ₂ (CO ₂ /H ₂ S>20)	Depends on CO ₂ partial pressure	

A review of a wide number of field cases reports quantitative information about sour weight loss corrosion and proposes possible mechanisms. Fluid corrosiveness is classified into three categories, from a negligible corrosiveness which constitutes about 40%-50% of the cases (both in oil and gas production), to a moderate one (typically within 1 mm/year) in the most of other cases, and lastly to a very severe corrosion (10 mm/year, even in apparently mild conditions) in a few cases. The flow velocity and flow regime are shown to be the most leading factors of the transition between negligible and intermediate and severe corrosion categories. Very severe corrosion cases require "pit promoters" (sulfur, oxygen, and bacteria) and a "galvanic effect" with surrounding non-corroding surfaces. On the other hand, the H₂S and CO₂ partial pressure as well as the pH or the H₂S/CO₂ ratio not influence the corrosion likelihood if the CO₂/H₂S ratio is lower than 20.

6. Discussion

Different types of corrosion environments need different measures in order to mitigate the metal loss phenomena and consequent failures. Both the material composition of the product and the product fabrication method are important in corrosion behavior of the

metals. For example, for flat-rolled carbon steel the inclusion places can be the HIC/SWC initiation points. Hence, for this type of material when used in sour service related HIC/SWC evaluation tests should be done (NACE MR0175, 2001). Chrome is very important element for CO₂ corrosion control and about 0.5-1% Chrome can substantially improve the CO₂ corrosion rate of the material. Other elements which can enhance the resistance of material against CO₂ attacks are including Nickel, Molybdenum and Cobalt. However, the optimum selection of the material is not enough for corrosion control. There are other supplementary methods that can mitigate different types of corrosion. Using inhibitors such as glycol and methanol can reduce the rate of corrosion up to 90%. However, inhibitors cannot relief the SSC type failures. Table 3 indicates the actions which normally are taken against the most common corrosive media. In addition to information provided in Table 3; these rules also should be considered in material selection for different situations.

- Metallic coatings (electroplated and electroless plated), conversion coatings, plastic coatings and linings are not acceptable for preventing SSC (MR0175, N.S., 2002).
- Overlays applied by thermal processes such as welding, silver brazing, or spray metalizing

systems are acceptable if they comply with one of the following requirements (MR0175, N.S., 2002).

- Quenched and Tempered and Tempered products have better SSC resistance (EFC-16., 2009).

7. Conclusion

In this paper, the most common corrosion problems in upstream facilities of Iranian Central Oil Fields (I.C.O.F) are discussed. The corrosion mechanisms are described and the special strategies which experts in the I.C.O.F are using during material selection process are elaborated. According to the above discussion H_2S and CO_2 are the most corrosive media in oil and gas fields. While H_2S leads to localized damages; CO_2 causes a variety of problems such as localized or general corrosion. However; H_2S induced cracks are very dangerous and mitigation is much critical for this type of corrosive media.

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JOURNAL OF GAS TECHNOLOGY

Volume 7 / Issue 1 / Summer 2022 / Pages 70-85

Journal Homepage: <http://jgt.irangi.org>

Simulation of the Natural Gas Pipeline Explosion by Using PHAST Software and Investigation of Line Break Valve's Effectiveness

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ARTICLE INFO

ORIGINAL RESEARCH ARTICLE

Article History:

Received: 14 June 2022

Revised: 19 August 2022

Accepted: 15 September 2022

Keywords:

Pipelines, Gas

PHAST

Automatic valve

Line Break Valve (LBV)

Consequence

ABSTRACT

Two points need to be taken into consideration regarding buildings built around gas transmission pipelines in Iran, first, the density of the buildings and second, the distance from the axis of the pipeline. These values are determined by standard tables IGS-C-SF-015. Nevertheless, determining the two mentioned factors is not enough to determine the risk level of threats caused by gas pipelines explosion. The best way to calculate the risk level that threatens buildings around pipelines is by using computer calculations such as PHAST software to estimate the consequences of accidents and analyze the results based on natural accidents. However, it is worth mentioning that the PHAST software also cannot calculate the effects of soil in the explosion of burial pipes. Hence, the simulation by PHAST for an explosion-exposed gas pipeline can be a basis for other evaluations. After determining the appropriate consequence modelling, the effectiveness of using equipment that can reduce the explosion's consequences is also investigated. In this paper, after logical modelling for the real explosion, the effectiveness of a standard protective device in gas pipelines called Line Break Valve (LBV) for reducing the explosion's consequences is measured. At first, the probability of the LBV functioning at the time of the explosion is checked. Subsequently, by the diagram, the consequences of the accident for two modes of operation and non-operation of the LBV system are displayed and compared with each other. Ultimately, for the simulated mode, it is observed that the correct operation of the LBV system could reduce the accident consequences by more than 60%.

DOR: [20.1001.1/jgt.2023.555757.1001](https://doi.org/10.1001.1/jgt.2023.555757.1001)

How to cite this article

M. Doustmohammad, S.M. Mirhosseini, E. Zeighami, H. Lajvardi, Simulation of the Natural Gas Pipeline Explosion by Using PHAST Software and Investigation of Line Break Valve's Effectiveness. Journal of Gas Technology. 2022; 7(1): 70 -85. (https://jgt.irangi.org/article_707113.html)

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Available online 22 September 2022

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1. Introduction

Gas production and transmission need to be associated with three factors: safety, cost and sustainable development and inevitably to manage this vast and developing network, arrangements require to be made to balance these factors. The importance of safety and coordination with other factors in gas pipelines is displayed in (Figure 1) (Antaki George A., 2003).

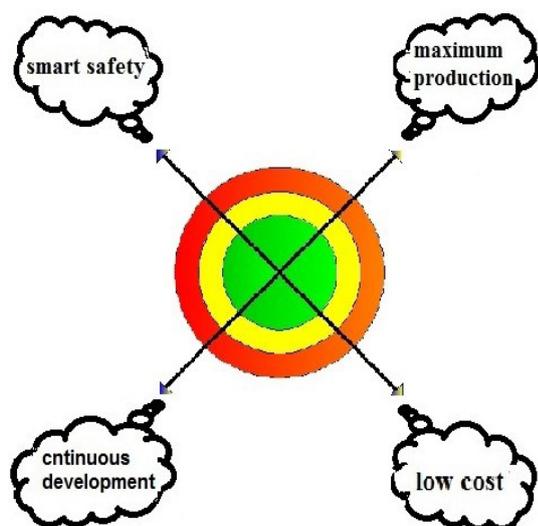


Figure 1. Main factors of Efficiency (Antaki George A., 2003)

Risk calculation is the conclusion from the probability of an incident occurring and the consequences of the incident. For only one type of threat (ASME B31.8S, 2020):

$$Risk_i = P_i \times C_i \quad (1)$$

C = failure consequence

P = failure likelihood

It is necessary to determine the values of C and P as much as possible to know the interaction between the environment and the gas pipeline on each other. (Muhlbauer, W. Kent, 2004)

The location class is defined based on human communities and buildings around the lines. According to the location, classes are determined by the thickness of the pipe and the distance between the valves. (ASME B 31.8 standard, 2022). Nonetheless, after 2018, replacing the pipe with a higher thickness is no longer necessary to upgrade the location class. (PHMSA, 2018)¹. Furthermore, ASME², explicitly states that the efficiency of automatic valves for risk calculations is not considered, but this effect can be calculated and considered by experts³. Moreover, PHAST software alone cannot consider the effectiveness of the automatic shut-off valve. Meanwhile, when an accident occurs in the gas pipeline, the speed of gas flow interruption is essential⁴ (FEMA, 2003). Common methods for determining the safe distance from the pipeline axis are:

- Potential Impact Radius (PIR) formula
- Iranian Gas standard (IGS-C-SF-015)
- Software

In this study, the safe distance for the gas pipeline (which has had an accident) is calculated and checked from all the above three methods and for the first time, it has been tried to identify the effectiveness of the LBV system and then its effect in the gas pipeline risk assessment.

(Figure 2) illustrates a schematic of the incident. Around 11:45 on 10 September 2010, during the implementation of the 48" Turkmenistan-Sangbast pipeline, this line needed to pass from under the first and second 36" gas lines Sarkhes-Mashhad, due to the fall of a side-boom on the Second line, a bursting has occurred. The gas leak covered the entire workplace, and then the explosion killed 16 people, injured 14 people, and destroyed the machinery and equipment.

1. PHMSA have suggested that performing PIMS where class locations have changed due to population increases would be an equally safe but less costly alternative to the current requirement of reducing pressure or replacing the pipe

2. ASME B31.8/846.2.1-d

3. ASME B31.8S-2020-5.5(b) (1)-Subject Matter Experts (SMEs).

4. When a gas pipeline explodes, one-third of the chemical energy is released at the initial explosion, and the remaining two-thirds is released slowly. Detonation products mix with air and burn. On the other hand, prolonging the leak time too much can affect some areas that were not damaged at the initial moment of the explosion. Therefore, from periodically, there is a possibility that the second part of the incident will cause far more significant consequences than the initial explosion.

2. The incident

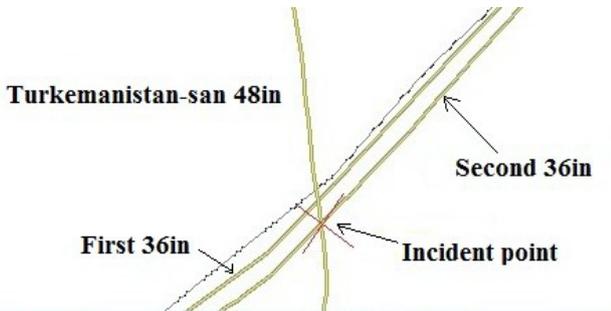


Figure 2. Location of the blast site

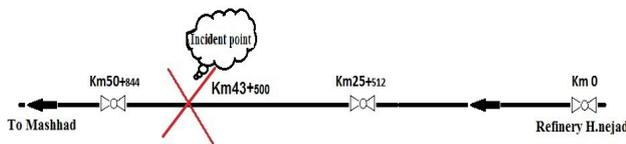


Figure 3. Schematic of the LBV's

(Figure 2) and (Figure 3) illustrates a schematic of the incident. Around 11:45 on 10 September 2010, during the implementation of the 48" Turkmenistan-Sangbast pipeline, this line needed to pass from under the first and second 36" gas lines Sarkhes-Mashhad, due to the fall of a side-boom on the Second line, a bursting has occurred. The gas leak covered the entire workplace, and then the explosion killed 16 people, injured 14 people, and destroyed the machinery and equipment.

- The distance between two 36" lines is about 16m.
- The 48" pipeline channel was about 4 meters deep and 3 meters wide.

- The side-boom is about 70 tons.
 - At 11:54 a.m., the LBV valve at 51 km was closed immediately after the explosion.
 - At 12:18, the valve of zero kilometer of the new line 36" was closed by manpower.
 - At 13:35, according to witness reports, fire could be observed at the scene.
 - At 13:56, from 51 km gas purged (open vent valves and gas vented into the environment)
 - At 14:05, closed valve at 25 km, and the purged the line.
 - The area under explosion is about 10^5 m^2
- (Tables 1 to 3) explain the details

Table 1: Gas Components 36" Liness

Component	Mole percentage
Nitrogen	0.56
Carbon dioxide	1.00
Methane	97.66
Ethan	0.61
Propane	0.10
Isobutane	3.47
0.01	0.78
Normal butane	0.03
Isopentane	0.01
Normal pentane	0.02

Table 2: Properties of air and natural gas

Natural Gas	Air	Specifications
0.688	1.205	Base density (kg/m^3)
1.304	1.4	Specific heat ratio
1700	717.3	Heat transfer coefficient in constant volume (J/kgK)
288.2	288.2	Base temperature (K)

Table 3: Explosion Incident Modeling Information

Gas pipeline specifications	Description	pipe specifications	Description	Conditions	Description
Gas pressure	930-1000 Psi	Material and standard of the pipeline	API 5L X 60	Distance from gas control valves	18 km from upstream and 8 km from downstream
Gas temperature	313 k (40 C)	Pipe thickness	0.562 in	How the incident happened	Perforation, severe leakage and explosion, respectively
Gas flow	35, 280, 770 m ³ /day	Location Class	B	Explosion profile	JET fire & Detonation
Ambient air profile at the time of the incident	2010 sept 10, Friday 11:45 PM	Pipeline distance to ground level	4 meters - in free surface mode	Approximate radius of degradation	180 m
Environment temperature (T)	30 C	Distance between existing pipelines	18.6 m - several parallel lines	Enclosed in soil / free surface	free surface
Relative humidity	17%	Effective pipeline length	51 km	air pressure (P)	91kPa

3. Potential Impact Area(PIR)

One method to calculate the consequences of a gas pipeline's possible incident and to estimate the area affected by the damage caused by it. Its pressure is not more than 1450 psig (10 MPa), and its temperature is not less than 0 °C (32 F). Formula (2) can be used to estimate the explosion radius: (ASME B31.8S, 2020)

$$r = 0.69d\sqrt{P} \quad (r = 0.00315 d\sqrt{P}) \quad (2)$$

While:

d = outer diameter, in. (mm)

P = (MAOP) Maximum allowable working pressure, psig (kPa)

r = potential effect radius, ft. (m)

Using the formula (2) the explosion radius for line 36" in pressure 1000psi:

$$r = 0.69 \times 36 \times (\sqrt{1000})$$

$$r = 785.51 \text{ ft} = 239.423 \text{ m} \approx r = 240 \text{ m}$$

In (Figure 4), which is adjusted according to the formula (2), for gas pipe 36" in 7000kPa (1000psi) is approximate radius 243m.

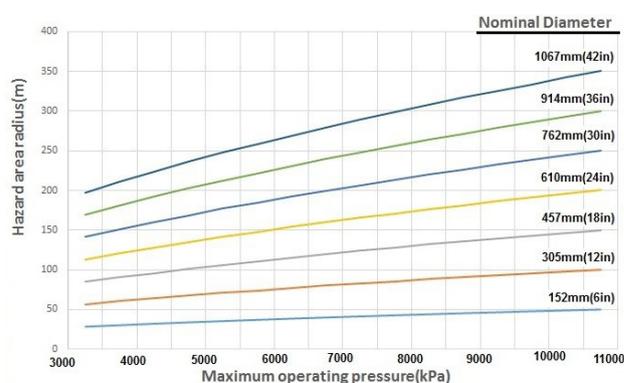


Figure 4. Proposed Hazard Area Radius as a Function of Line Diameter and Pressure (K. Moore, 2002)

4. The Legal Distance

Although increasing the thickness has an effect on reducing the probability of an incident and although increasing the thickness reduces the probability of an incident and thus reduces the risk, it has almost no effect on the consequences. Due to population growth and industrial development, legislators should consider a safe distance from the pipeline axis according to the type of buildings. Risk calculations can help them determine this distance. According to the IGS

standard, the maximum distance considered safe from a 36" gas pipeline with a design pressure of 1050 psi is 200 meters. In accordance with (Table 4) and by comparing this distance and

the incident distance calculated in section 3, it can be seen that the maximum legal distance considered for the pipeline is 40 meters less than the calculated PIR Distance.

Table 4: Safety zone for prohibition of construction from the pipe axis (meters) for a nominal diameter of 32 to 38 inches

Type of buildings	Maximum allowable operating pressure	Design coefficient			
		0.72	0.6	0.5	0.4
Buildings are a gathering place and dangerous	400-1050 (lb/in ²)	200	200	40	20
For ordinary buildings with design factor D	900-1050 (lb/in ²)				20
For ordinary buildings with design factor C	900-1050 (lb/in ²)			40	
For ordinary buildings with design factor B	900-1050 (lb/in ²)		55		
For ordinary buildings with design factor A	900-1050 (lb/in ²)	70			

Summary of values in Tables 1-5(IGS-C-SF-01) for 36" pipe.

5. Software

The consequence or "leakage factor" calculation depends on two factors.

1. Thermodynamic and composition properties of gas (up/downstream) in the pipeline
2. The environment around the pipeline

Due to the large number of variables, the scope of their changes, and the complexity of the interactions of these two factors, the best way to consider the above two factors in consequence calculations is to use computer software. The following four steps need to be taken in order to evaluate the consequences of an incident by using PHAST software: (Colin, Hickey, 2016)

1. Scenario determination
2. Possible mode selection
3. Incident modelling
4. Damage assessment

Preferably, it is necessary to consider a suitable and probable scenario(s) to simulate an incident. To this aim, a real accident can be used as a suitable scenario and as a basis for selecting other scenarios to localize the basic

risk assessment model. In this paper, as much as possible, the selected variables for simulation are tried to be similar to those observed in the real incident of the Sarakhs-Mashhad line. After that, the obtained results are used for two purposes: To compare the consequences of the real scenario with other possible scenarios and to identify and calculate scenarios that PHAST software cannot calculate. Such as the effectiveness of LBVs in gas pipelines. Choosing this incident is suitable for simulation because the desired software:

- Because the PHAST cannot dedicate models for underground pipe rupture (Karim, OSMAN, 2016)
- Absence of structures in the radius of propagation of the incident wave
- Lack of significant vegetation around the pipeline
- The surrounding environment is relatively flat and without obstacles

Challenges of incident simulation:

Although the above comparative advantages increase the probability of convergence of modelling results with the severity of the actual incident, it is impossible to accurately match the

consequences of the incident with the software results.

- It takes over 3 hours to see the flame until it is extinguished. Changing the weather conditions, such as changing the angle and intensity of wind, is possible. This can cause the radius of the incident to be asymmetric, especially at distances far from the incident site.
- Purging the gas from the beginning and end points may have reduced the severity of the consequences of the accident to some extent
- Hypotheses: The following assumptions are considered to minimize the difference between the simulation results and the real accident outcome:
 - based on the available evidence, the area under the influence of damage caused by the incident is determined, and then the
 - Radius of the incident is considered based on that area.
 - The incident boundaries are considered symmetric, and the incident severity is based on this symmetric distance.
 - The radius of the incident is considered according to the most dangerous severity of the effect observed at the scene of the incident

Determining the incident scenario:

In PHAST software, depending on the type of facilities and materials used in them, different scenarios are considered for different types of incidents:

- Release of toxic substances
- Explosion
- Ignition

In general, for a pipeline carrying natural gas flow, due to its non-toxic/non- allergenic nature, for natural gas (which mainly contains methane), incident scenarios are considered only based on explosion and ignition.

(Table 5) shows all the possible states of the accident and the probability of each. In such a way, the states with a low probability of occurrence are marked with yellow color, the states with a high probability of occurrence are marked with green color and the impossible states are marked with red color. BLEVE, CE modes for explosion and Spherical fire and Pool fire for ignition are likely to occur only if the fluid is liquid, and dust explosion mode requires the presence of flammable dust particles in the air (ISSA, 2004). So what might happen is:

- Vapor Cloud Explosion (VCE)
- Flash Fire
- Jet Fire

Table 5: Probability of natural gas accidents

FIRE	EXPLOSION
FLASH FIRE	VCE
FIRE BALL	BLEVE
JET FIRE	CE
POOL FIRE	DUST

High probability
Likely
impossible

It is essential to mention that Flash Fire cannot release significant energy and does not create a pressure wave. VCE is created in conditions where: closed spaces, spaces with sufficient obstacles or gas flow in the atmosphere can become "gas clouds". The explosion radius in the VCE mode is caused by a balanced and explosive mixture of gas and air, which largely depends on the environmental conditions in the open space. (Naemnezhad, Abolfazl., 2017) However, according to the remains and observations made from the incident area, it is observed that the primary damage was caused by fire. Ultimately, it is necessary to perform a simulation for three possible accident situations.

Gas leakage and determination of different states and assumptions:

In determining possible scenarios caused by gas, one essential factor in determining the shape and amount of leakage. According to objective observation, the initial leakage was due to a 70-ton side boom falling from a distance of 3 meters and falling on the pipe. The IGT / AGA formula needs to be used to calculate the amount of gas available and determine the approximate amount of flammable or explosive gas¹. The amount of gas available in the distance from the place of rupture of the pipe to the valve 51 km downstream (distance about 8 km) in case of immediate operation of the LBV is approximately 387,453 m³(actual value is 368,143 m³), which in case of a complete rupture in the first moment, time of discharge are about 140s to 350s, according to formula (3). (A.G.A, 2020)

$$T = \frac{(0.0588)(P_1)^{1/3}(G)^{1/2}(d^2 LF_C)}{d_b^2} \quad (3)$$

T Discharge time (minutes)

$P_1 = 930$ (PSI) Gas pressure

$G = 0.688$ Gas density

$d = (36-2 \times 0.562)$ Gas density

$d_b = d$ The ID of drain pipe²

$L = 8 \text{ Km} = 5$ (mile) The length of the discharge pipeline

FC Valve clotting factor is considered between 1 and 2.5

$$\frac{(0.0588)(930)^{1/3}(0.688)^{1/2} \times (5) \times (34.876)^2 \times 1}{(34.876)^2} = 2.38$$

$T = 138 \text{ s}$ $Fc = 1$

$T = 345 \text{ s}$ $Fc = 2.5$

A comparison of the calculated time with the actual conditions shows that the explosion and complete cutting of the pipe section did not occur in the first minutes. On the other hand,

considering the size and strength of the pipe in (Table 3), it seems unlikely that a pipe with a yield strength of 60,000 psi and its joints have been hydrostatically tested up to 1150 psi, While the two ends of the pipe are also semi fixed, had been fully ruptured in the early moments of the accident. Consequently, we assume the average upward leakage rate in the initial moments of the side-boom fall and then compare the results with the observed objective consequences.

The intensity of the pressure drop has caused the LBV to be activated at 51 km. The corresponding amounts of gas are discharged from each of these points. The minimum gas output from the upstream incision site (due to the closing valve and discharge from 0 and 25 km) by formula 4 is estimated at 1,002,548.955 m³ (actual value is 936,689 m³). (A.G.A, 2020)

$$V_b = V \times (T_b/P_b) \times (P/T) \times (Z_b/Z) \quad (4)$$

V_b Gas Value (m³)

$V = 15405 \text{ m}^3$ Pipe value

$T_b = 519.67 \text{ R}$ Base temp

$P_b = 1.013$ Base pressure

$P = 64 \text{ bar}$ Gas pressure

$T = 563.67 \text{ R}$ Gas temperature

$Z_b = 0.998429$ Base Compressibility factor

$Z = 0.893594$ Compressibility factor

According to the values of Tables 1, 2, and 3, it is possible to calculate the maximum rate of gas exit from the incident pipe and determine the required software values by converting the units. Average gas passing through the pipeline involved in the incident: Total volume of available gas: is the sum of exhaust gas from the sides of the rupture:

$$35,280,779 \frac{\text{m}^3}{\text{day}}$$

is the sum of exhaust gas from the sides of

1. The inaccuracy of the pressure gauges and the long length of the gas pipeline creates the possibility of the inaccuracy of the pressure, so adjusting the numbers after each simulation according to the results and following the available evidence.

2. The inner diameter of the drain/vent pipe, which is equal to the inner diameter of the pipe in the case of full rupture

the rupture: Maximum gas outflow rate

$$368,143 \text{ m}^3 + 936,689 \text{ m}^3 = 1,304,832 \text{ m}^3$$

Maximum gas outflow rate

$$35,280,779 \frac{\text{m}^3}{\text{day}} \times 0.688(\text{kg}/\text{m}^3) = 23,567,554.3 \frac{\text{kg}}{\text{day}}$$

$$= 272.77 \text{ kg}/\text{sm}^3$$

Correspondingly, depending on the side-boom's hit, the release angle was considered vertical (of course, there was a possibility of changing direction in the following moments)

The results of PHAST software calculations for the two modes of closing the LBV in the 60s (ideal mode) and the state without operation of the LBV to closing by human resources (similar occurred in the actual incident) together are compared and then compared different weather conditions with existing (real) conditions. It takes at least 40s-50s from the explosion to close a 36" valve completely.

Explosion:

(Figure 5) and (Figure 6) show the actual geographical position around the explosion site, and the roughness of the earth's surface is displayed in specific radii, respectively.

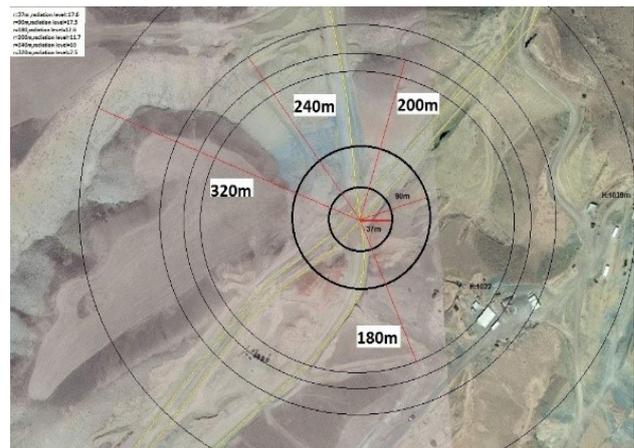


Figure 5. Geographical location

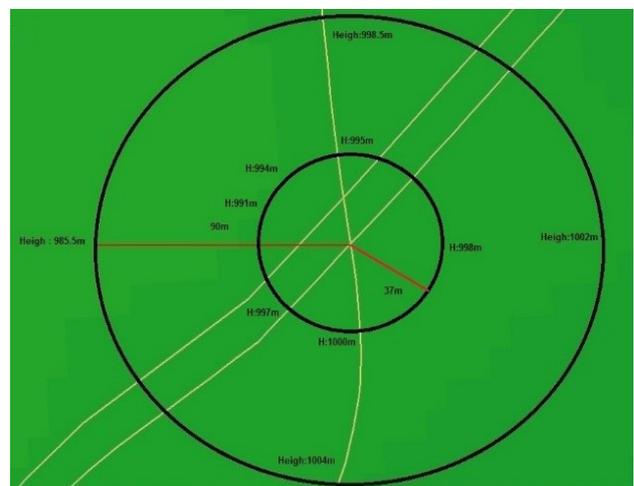


Figure 6. Changing ground levels

Table 6. damage Approximations (FEMA 426, 2003)

Incident Overpressure (psi)	0.15-0.22	0.5-1.1	1.1-1.8	1.8-2.9	Over 5	4-7	6-9	10-12
Damage	Typical window glass breakage	Minor damage to some buildings	Panels of sheet metal buckled	Failure of concrete block walls	Collapse of wood framed buildings	Serious damage to steel framed buildings	Severe damage to reinforced concrete structures	Probable total destruction of most buildings

It will be seen that the existing roughness is not significant enough, and It has no effect on the intensity of harmful factors (especially the intensity of radiation) caused by jet fire. The destructive effects of the explosion are due to the increase in pressure. The severity of damage in terms of blast pressure is according to (Table 6) (KINNEY & GRAHM,1985). This table

shows that for increasing the pressure by more than 1 bar (14.504 psi), probable destruction of most buildings, nevertheless, even at lower pressures, damages are caused too. (Figure7 and Figure 8) show the explosion pressure distance above 1 bar and how to reduce it, respectively, for LBV that stays open for 3 hours and the state of LBV that closes within

the 60s after the incident. In the following, the severity of the incident for the two mentioned cases in the worst possible case is compared (Figure 9) and (Figure10)

A) Intensity of damage due to explosion

For the desired 36" line:

- Explosion radius when the valve is open: 108 meters (Figure 7)

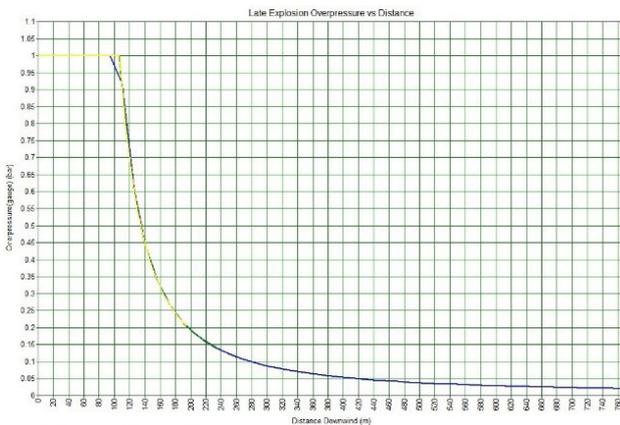


Figure7. The effect of over pressure (Explosion) when the valve is open

- Explosion radius when the valve is closed: 68 meters (Figure 8)

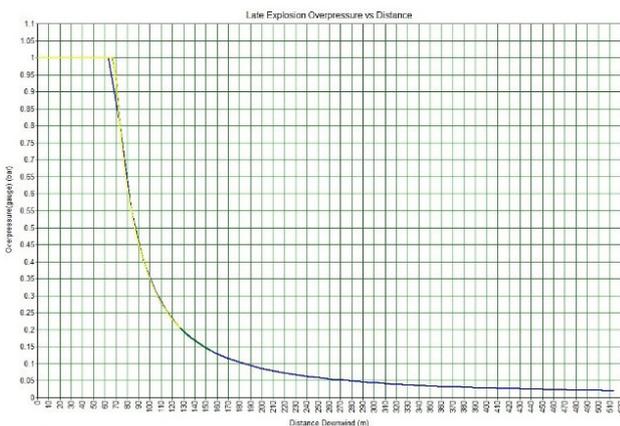


Figure 8. The effect of over pressure (Explosion) when the valve is closed

B) Worst possible explosion mode:

- The worst possible radius of explosion without valve operation (open valve in real time) (Figure 9) is about 190m to 850m.

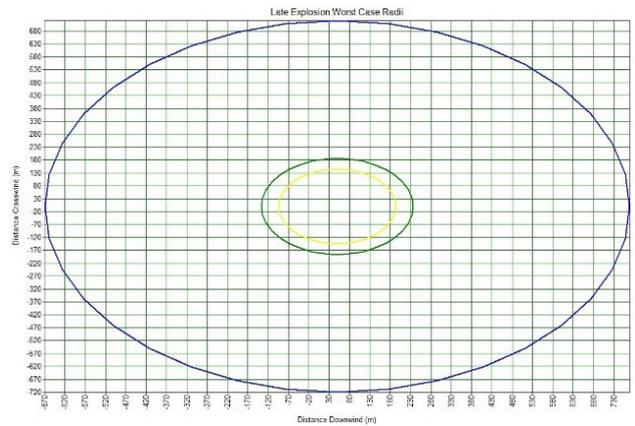


Figure 9. Worst possible explosion mode for opened valve

- The worst possible radius of the explosion, when the valve is closed in less than the 60s (Figure 10), is between 122 m and 520 m.

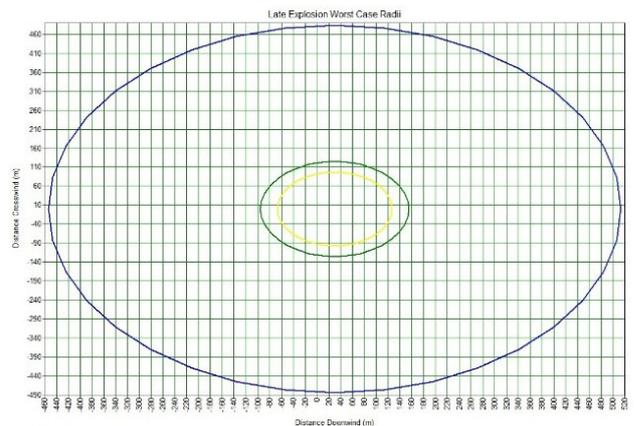


Figure10. Worst possible explosion mode for opened valve

Flash Fire:

The radius of Flash fire when the valve is open (Figure 11) is 20 m (for the amount of gas at the rate of mixing 4.4 ppm) to 54 m (for the amount of gas at the rate of mixing 2.2 ppm) and flash fire radius when the valve is closed (Figure 12), between 13 m (for the amount of gas at mixing 4.4 ppm) to 36 m (for the amount of gas at the rate of mixing 2.2 ppm) the mixing rate for continuous gas ignition starts from at least five ppm, damage at intervals calculated for Flash fire has much explosion modes. The explosion and Jet fire cover the destructive area of Flash fire.

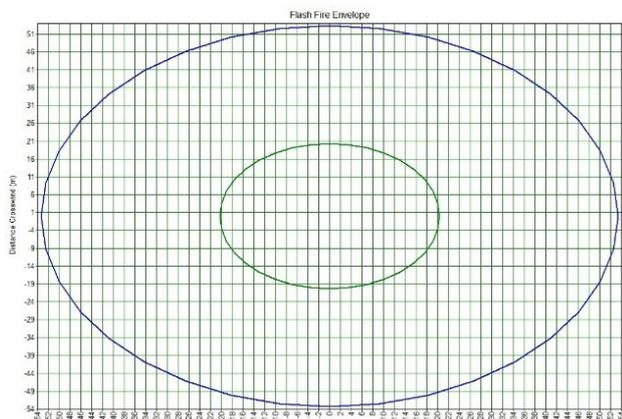


Figure 11. Flash fire radius for opened valve mode

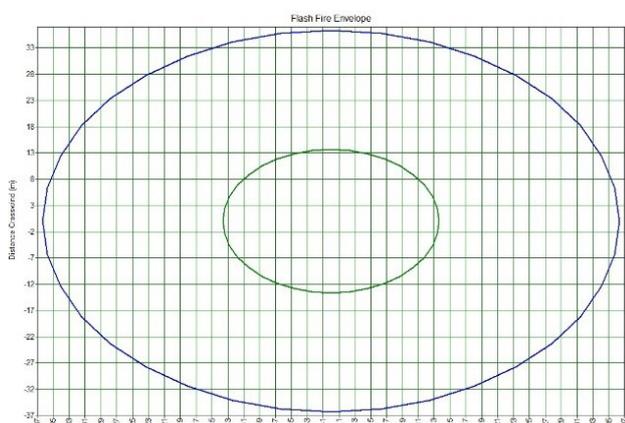


Figure 12. Flash fire radius for closed valve mode

Jet fires:

The approximate radius of the destruction effect can be obtained from (Figure13). This diagram is based on the experimental results of Jet fire destruction in the United States for sizes between 14" to 36" and pressure 575 psi to 1200 psi. (S. Haklar, James., Densnak, Robert.1999) For example, pressure of 1000psi, the burn radius will be:

$$BR = 680 \text{ ft.} = 207 \text{ m}$$

$$\text{Burn Radius (BR)} = (D^2 - (\frac{H}{2})^2)0.5 \tag{5}$$

D: Distance from the flame center to the observer

H: Flame height

Using Formula (5) and the approximate and hypothetical minimum value *D* = 220 m, the value *H* = 150 is calculated. Comparing the amount of minimum height calculated for the

flame and the changes in height and terrain features from (Figure 6) it results that the flames are so high that they have been able to emit their thermal radiation beyond the terrain. On the other hand, some eyewitnesses have claimed that they have seen the light from the incident flame from a distance of 64 km, in which case the height of the flame can be considered much higher than the estimated and minimum calculated value, and this means that terrain features could not create a significant obstacle in the development of ignition radiation. According to the incident report, the gas flow and, in other words, the ignition fuel supply continued for about 3 hours.

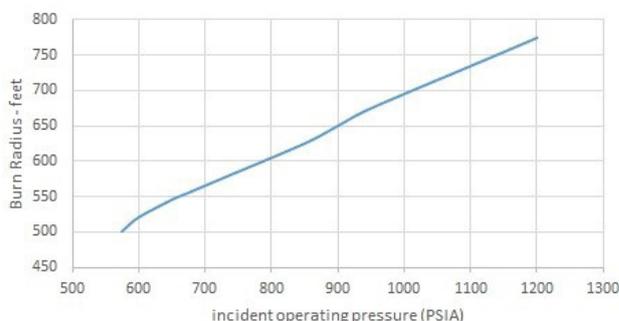
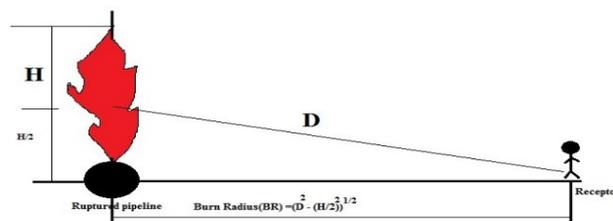


Figure 13. Radiation degradation of flame radiation

Intensity of radiation effect (Heat flux value):

The extent of the damage for different amounts of heat flux is shown in (Table 7). (Mark J. Stephens, 2002) the intensity of the effect in the closing mode of the valve (Figure 14) up to a radius of 105(m) is 12.5 (yellow diagram) and up to a radius of 345 (m) is 4 (green diagram), and the intensity of the effect in the open state of the valve (Figure 15) is up to a radius of 180(m) is 12.5 (yellow diagram) and up to a radius of 520 (m) is 4 (green diagram). Immediate operation of the automatic valve (in 60 seconds), and the area under damage was 3.5 hectares.

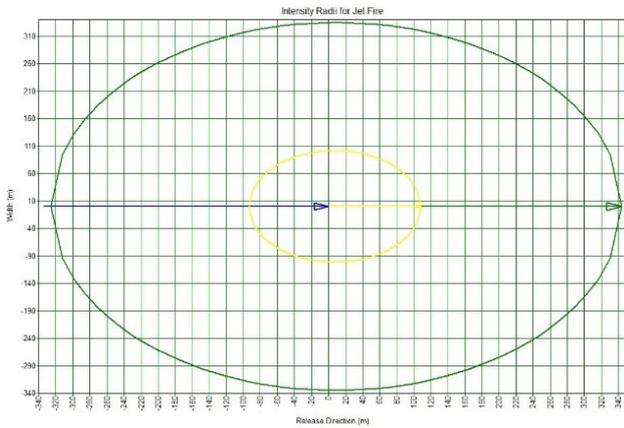


Figure 14. Jet fire effect for closed valve mode

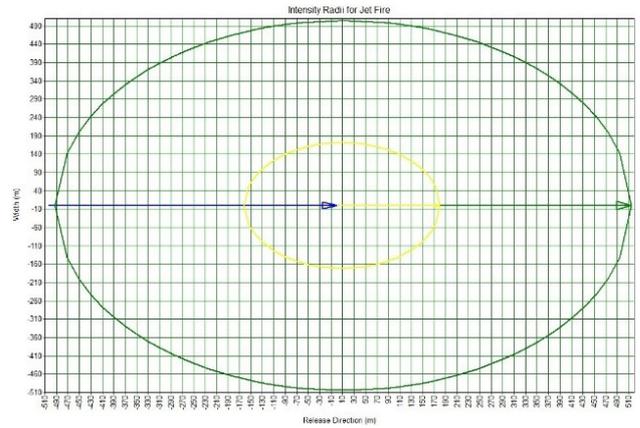


Figure 15. Jet fire effect for opened valve mode

Thermal radiation changes in radial distance:

Table 7. Vulnerability to heat (Mark J. Stephens, 2002)

Thermal radiation (kw/m ²)	1.2	2.1	4.7	6.3	9.5	12.6	15.6	23	35	37.5
Description	Received from the sun at noon in summer	Minimum to cause pain after 1 minute	Will cause pain in 15-20 second and injury after 30 s	Serious injury after 1 minute but the body is protected by clothing	Damage and the possibility of ignition in a few seconds	Deadly damage and heat generation to the extent of wood flame	Damage to structures and low chance of taking refuge	Damage to unprotected metal equipment	Cellulose material catches fire	Any equipment will be damaged

(Table 7) shows the intensity of damage in the ignition state is due to the intensity of the radiation effect. For closed valve mode (Figure 16), the maximum radiation intensity is 16.5 kw/(m²) at 40 m and for opened valve mode (Figure 17), 18.5 kW/(m²) at 60 m. for closed valve mode at radius of 110 m, the amount of radiation intensity is 12.3 kw/(m²), and if the valve is left open, the same radiation intensity reaches a radius in 180 m.

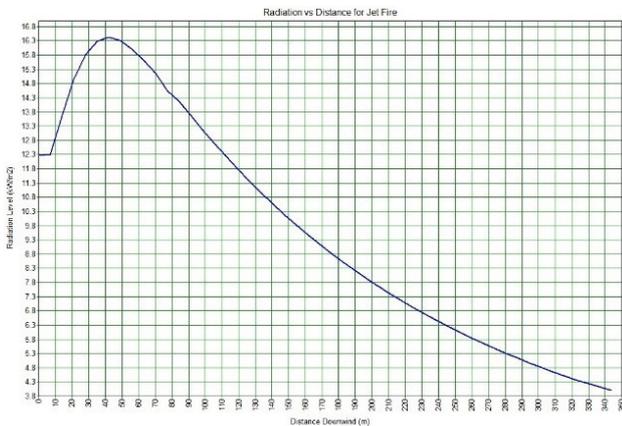


Figure 16. Max of intensity is 16.5(kw/m²) for closed valve mode



Figure 17. Max of intensity is 18.5 (kw/m²) for open valve mode

6. The effect of atmospheric conditions

In (Figure 18), the explosion radius diagram from the increased pressure. In (Figure 19), the explosion worst state diagram and (Figure 20), the intensity of the immediate fire effect diagram, are shown for different atmospheric conditions so that for condition (1.5D- blue

diagram), the radius of wave can able extended to 2500 m (Figure 18). The possibility of such weather in the incident area and at the time of the incident is very far from conceivable. Nevertheless, this example was raised to determine to what extent a lack of attention to probable weather conditions can affect the outcome assessment and ultimately distort risk management.

This means more probable conditions should be tried according to reliable weather information for a reasonable estimate. On the other hand, the effect of destruction in the real case has been seen up to a distance of about 2000 meters. However, for the reasons mentioned in Section 5, this distance has been avoided as a basis for comparisons. The radius of ignition, which has caused severe injury, has been considered the radius of the accident. That is, the potential space of severe injuries is also considered to manage the risk and consider the severity of the consequences. (Figure19) shows that in addition to the radius of the explosion, the gas mass’s displacement before the explosion’s moment can also be another factor in the propagation of the blast wave. (Table 8) summarizes the results of software surveys for different weather conditions and the impact of automatic valve performance.

(Figure 20) shows atmospheric conditions that could increase the instantaneous fire radius by up to 500 times. However, this atmospheric effect on the dimensions of the accident outcome is specific to the flash fire (Shuran Lyu, 2019).

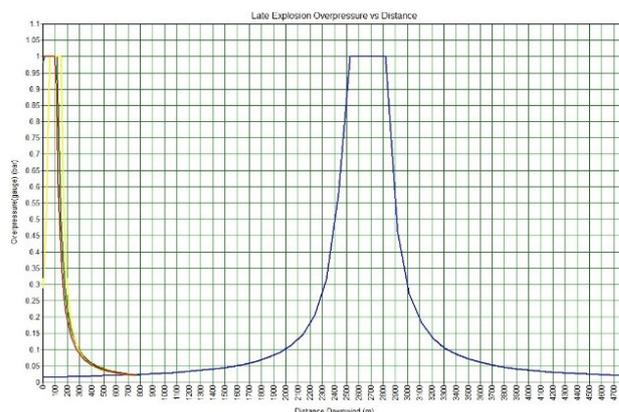


Figure 18. Increased explosion pressure for different types weather

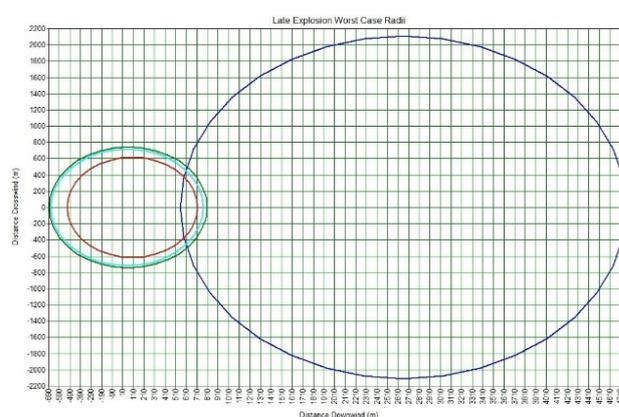


Figure 19. Worst Explosion Mode for different types weather

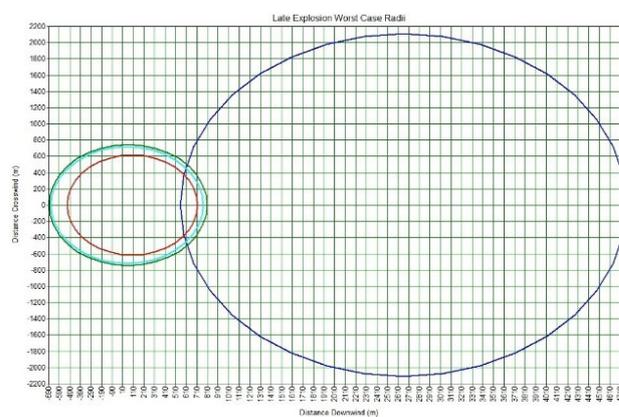


Figure 20. Flash fire for different types weather

Table 8: Comparison of weather conditions

Row	Degradation parameters (Explosion and ignition)	weather				Reduction of outcome if the valve, km25 is closed (%)
		1.5F	5D	1.5D	Real	
1	Damage radius due to increased pressure wave (m)	38	2500	150	110	108
2	Worst Explosion Radius (m)	36	4750	710	810	190 -760
3	Flash fire radius (m)	35	1050	10	10	20
4	Jet radius (m)	42	660	175	165	180
5	Thermal radiation (kw/m ²)	17.5	19.5	42	18	20
6	Damage area (104 m ²)	65	136	9.5	8.5	10

7. The effects of LBV

One of the few measures that can be taken after the explosion to reduce the scope of the damage and the consequences of the accident is to limit the gas flow of the pipeline or gas transmission network on both sides of the incident up/downstream. In this incident, the upstream LBVs can operate automatically and cut off the gas flow after detonation. LBV can operate with the help of a fully mechanical mechanism. In the previous diagrams, the effect of this malfunction was compared with the ideal mode, i.e. the operation of this system and the closing of the upstream valve in less than 60 seconds. Another critical issue is the reliability of the operation of this system and, ultimately, the possibility of closing the valve at the time of the incident, for the possibility of operation of this system. The most critical parameter that must be considered is the Determination and adjustment of LBV, proportional to the pressure drop rate (PDR) of the gas pipeline when the accident occurs because, outside the PDR range, the LBV system is not able to recognize the accident and is not able to cut off the flow.

(Figure 21) shows the PDR at the downstream valve location, less distant from the incident site(8km), is significantly higher than the upstream valve location, located 18 km from the incident site (The derivative of the yellow graph is greater than the derivative of the blue graph), in the first 100 seconds after the explosion, there is no noticeable change in the upstream gas pressure due to the effect of compression forces of the gas inside the pipe, and this will be a reason for the very low probability of closing the upstream valve in less than 60 seconds. Closing the valve during the mentioned time significantly reduces the explosion consequence, so with the existing automatic shut-off mechanism, such a performance is practically impossible. The start time of the valve is at best after 100 seconds, and the cut-off time from Equation (6) is calculated:

$$100s + \text{valve operation time (VOT)} = \text{flow interruption time} \quad (6)$$

100s: Delay time until receiving PDR signal

VOT: According to the manufacturer's instructions

The proper closing time for a 36" valve is usually between 30 and 50 seconds, and according to Equation 6, the minimum shut-off time is estimated at 130 to 150 seconds.

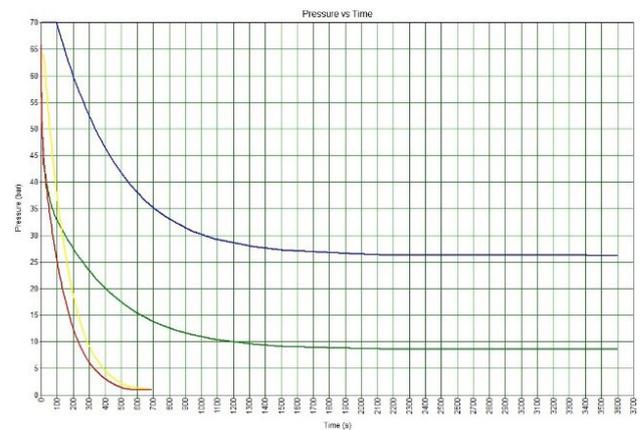


Figure 21. PDR for open valve mode

(Figure 22) shows the rate of PDR at the upstream valve location over time after the explosion.

After the explosion for 100s, there is no pressure drop at the 25 km valve, then from 100s to 150s, the maximum PDR is slightly more than 6 bar/min (drop is 6 bar in 55s). According to IGS-M-IN-304 standard, the allowable range of pressure drop rate is between 0.5 to 6. However, it is observed that placing the LBV setting at point 6 is the limit of the simulated explosion and considering that the feeling of PDR due to the explosion in the existing system is mechanical; Firstly, its precise adjustment is not possible, and secondly, its performance reliability is low compared to digital and electronic systems. Accordingly, a set point of 6 bar/min increases the risk of LBV performance at the time of the accident. Regardless, adjusting the LBV in the PDR range of less than 4, and if the system service is performed regularly and accurately, the correct operation can be imagined for the desired automatic valve.

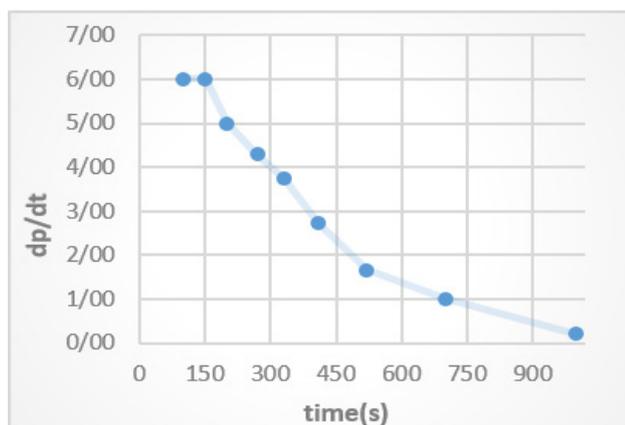


Figure 22. Pressure drop rate (PDR) over time (after 100 seconds)

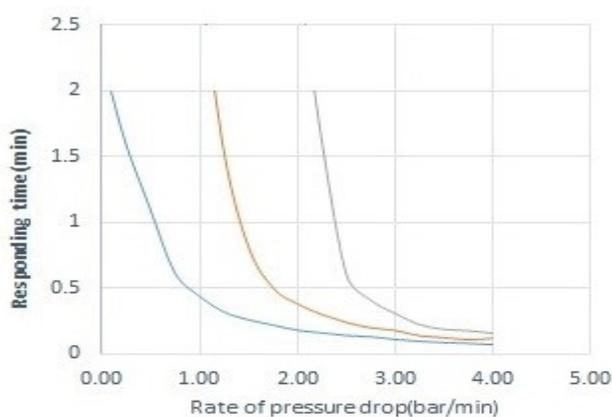


Figure 23. Example of a SCHUCK adjustment chart (MANUAL, 2008)

In (Figure 23), for this model of automatic valves, the appropriate diagram with a working pressure of 1000psi is diagram No. 2 (middle). If the PDR of 2 (bar/min) is considered for the operation of the LBV, according to the manufacturer's instructions, by receiving the cut-off response in time 22 s when adjusting and ensuring the correct operation of the automatic valve, then at the time of the incident (time 150s to 450s), the possibility of automatic valve operation was considered in the first minutes (INSTALLATION OPERATING MANUAL MAN712. 2008). In fact, the main point in this section is to understand the concept and importance of determining the gas PDR at the time of the incident in order to suitable automatic shut-off system and adjust the set point for these valves by line designers and notify operators and Consider an automatic shut-off system with a high performance factor

Because, as can be seen in the real incident, not paying attention to this issue could cause the inefficiency of the automatic valve between the 50 km road and increase the destructive consequences of the incident. The choice of a mechanical system with a lower performance coefficient than digital systems and remote control by the designer and defects in service and maintenance of the way valve by the operator are the main factors in the non-operation of the upstream valve (25 km valve). Furthermore, at the time of construction and during the entire period of operation, the costs of purchase, installation, service and maintenance for the new valve at the time of the incident have been paid.

8. Conclusions

1. The approximate radius of the real incident is 180m, and the leading cause of destruction is the jet fire, which is simulated as a perfect approximation by the software.
2. Currently, the maximum distance allowed for construction permitted by law for a 36" pipeline in accordance with location class 1 is 200 meters.
3. With the help of the calculation formula of the potential impact radius (PIR), the effect radius up to 240 meters is calculated and estimated.
4. The radius calculated by the software for the specific state of the real incident (based on environmental conditions, weather, Etc.) is estimated at 108m to 190m for the explosive state, and 180m for the jet fire, which is an excellent estimate of the simulation and the power of the software is mentioned.
5. Changing environmental conditions such as burying pipes, posts or more heights around the incident, the existence of facilities and buildings around the incident site and most importantly, changing weather conditions could significantly shift the

destruction radius.

6. The essential equipment that could reduce the amount of damage after the incident was the automatic shut-off valve, which according to (Table 8), could significantly reduce the consequences of explosion and ignition, so according to studies and the Installed LBV mechanism, the following results are obtained:
 - A) The probability of its operation during the first 100s of the leak, regardless of the model, type and quality of LBV used and based on the dynamics of the explosion, could be higher (or impossible).
 - B) If the performance of the upstream valves were set above the IGS-M-IN-304 standard (i.e. a PDR of 6(bar/min), the probability of their performance at the time of the incident would be very low.
 - C) According to the pressure drop rate calculated by the software at the valve at 25 km, it can be concluded that the dynamic conditions created by the explosion were suitable for LBV operation and, consequently, automatic shut-off system wear, lack of regular service, improper adjustment and other Reasons for wear and tear of the device and operation can be identified as the cause of malfunction of the valve at 25 km.
7. Identifying inefficiencies and replacing the LBV system with appropriate systems can significantly reduce the level of damage and consequences of the incident, reducing the level of risk and increasing productivity.
8. The costs for increasing the performance of automatic shut-off valves are much lower than the cost of changing the pipe and upgrading the class, so paying

particular attention to this issue is recommended to improve integrated management.

9. According to (Figure 1), it can be seen that the installation of an inefficient automatic shut-off system disrupts the integrated management of gas pipelines by reducing safety and increasing costs.

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انتخاب شرایط عملیاتی بهینه اقتصادی در چیدمان‌های پیچیده برج‌های تقطیر برای فرآیند تفکیک مایعات گاز طبیعی

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چکیده

استفاده از طرح‌های نوآورانه در طراحی فرآیندهای تقطیر چند جزئی به دلیل تعداد بالای متغیرهای طراحی کاری بسیار پیچیده است. فشار یکی از پارامترهای عملیاتی مهم در برج‌های تقطیر است و به‌طور مستقیم بر هزینه‌های عملیاتی و سرمایه‌ای تأثیر گزار است. تاکنون روش‌های بسیاری شامل روش‌های ابتکاری و بهینه‌سازی برای یافتن فشار عملیاتی بهینه برج‌های تقطیر ارائه شده است. از آنجاکه فرآیند تفکیک مایعات گاز طبیعی (NGL) یک فرآیند پرهزینه و پرمصرف از نظر انرژی محسوب می‌شود، طراحی و بهره‌برداری از این واحد فرآیندی تأثیر قابل توجهی در زنجیره تأمین محصولات پتروشیمی و کل مجموعه فرآوری گاز طبیعی می‌گذارد. در این مقاله مقایسه‌ای بین روش طراحی ابتکاری برج‌های تقطیر و روش بهینه‌سازی تصادفی به کمک الگوریتم ژنتیک برای طراحی چیدمان‌های ساده و پیچیده برج‌های تقطیر در فرآیند تقطیر چند جزئی به‌منظور طراحی فرآیند تفکیک مایعات گاز طبیعی صورت گرفته است. نتایج این پژوهش نشان می‌دهد که روش ابتکاری عملکرد سریع‌تری نسبت به روش بهینه‌سازی دارد اما در چیدمان‌های پیچیده برج‌های تقطیر با مقداری خطا همراه است. در مطالعه موردی صورت گرفته برای فرآیند تفکیک NGL نتایج حاصل از بهینه‌سازی توسط روش ابتکاری اختلاف ۴۰ درصدی در فشار محاسبه شده برای برخی از برج‌ها نسبت به روش بهینه‌سازی با الگوریتم ژنتیک نشان می‌دهد. این خطا باعث افزایش ۳ درصدی هزینه‌های سالانه چیدمان می‌شود که به دلیل خاصیت تجمعی خطا می‌تواند تأثیر قابل توجهی بر طراحی نهایی واحد گذاشته و حتی رتبه‌بندی نهایی چیدمان چیدمان‌ها را تغییر دهد.

واژگان کلیدی: تفکیک NGL، فشار عملیاتی، تقطیر چند جزئی، بهینه‌سازی فرآیند، قوانین ابتکاری

شناسایی ویژگی‌های کلیدی کیفیت در پروژه‌های خطوط انتقال گاز با استفاده از روش شبکه خزان

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چکیده

هدف اصلی این تحقیق، فهم‌شناسی ویژگی‌های کلیدی کیفیت در پروژه‌های انتقال گاز است. با به‌کارگیری نظریه سازه‌های شخصی کلی و روش شبکه خزان و همچنین انجام مصاحبه با ۲۰ مدیر و متخصص پروژه‌های انتقال گاز، ۲۸۴ سازه کیفی شناسایی شده است. این سازه‌ها با استفاده از تحلیل محتوا در ۴۰ دسته طبقه‌بندی و سپس با روش‌های آماری مورد تجزیه و تحلیل قرار گرفتند. با استفاده از تجزیه و تحلیل آماری ۹ ویژگی کیفی شامل، انطباق با استانداردها، شایستگی، تناسب در طراحی و مهندسی، نظارت مؤثر، اجرای صحیح، مطلوبیت، همگرایی، پاسخگویی و یکپارچگی شناسایی شد. این سازه‌ها به‌عنوان عوامل اصلی مؤثر بر کیفیت پروژه‌های انتقال گاز می‌باشند. در این مطالعه داده‌ها از پروژه‌های انتقال گاز انجام شده از ادارات کارفرما جمع‌آوری شده است. مطالعات بعدی نه تنها تعداد مصاحبه شوندگان را افزایش می‌دهد، بلکه مشارکت پیمانکاران در مصاحبه‌ها را برای دستیابی به نتایج جامع‌تری اعمال می‌کند. با توجه به شرایط حجم، دما و فشار، پروژه‌های صنعت نفت از حساسیت و اهمیت حیاتی برخوردار هستند. مدیران سازمان‌های پروژه محور می‌توانند از یافته‌های پژوهش حاضر برای ارتقای کیفیت و موفقیت پروژه استفاده کنند.

مطالعه حاضر جدید بوده و یکی از اولین موارد بررسی مفهوم کیفیت در پروژه‌های انتقال گاز است. این مقاله شواهد تجربی از تأثیر مثبت ویژگی‌های کیفیت بر عملکرد این‌گونه پروژه‌ها است و ادبیات مربوط به کیفیت را توسعه می‌دهد.

واژگان کلیدی: ویژگی‌های کیفیت، سازه، شبکه خزان، خوشه، انتقال گاز

مروری بر کاربرد فناوری نانو در تصفیه آب و پساب صنایع نفت، گاز و پتروشیمی

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چکیده

افزایش جمعیت و گسترش صنایع منجر به آلودگی و کاهش بسیاری از منابع طبیعی از جمله منابع آب شده است. استفاده گسترده از این منابع در مصارف خانگی، کشاورزی و صنعتی منجر به ورود آلاینده‌ها و محدودیت منابع آبی شده است. یکی از این صنایع، صنعت نفت و گاز و بخش‌های مرتبط با آن مانند پتروشیمی است که آلاینده‌های زیادی مانند فلزات سنگین، آروماتیک و غیره را وارد منابع آبی می‌کند. بنابراین توجه به استفاده صحیح از این منابع و راهکارهای تصفیه و استفاده مجدد از پساب ضروری است. روش‌های مختلفی برای تصفیه پساب از جمله لخته سازی، جذب سطحی، فیلتراسیون و غیره استفاده می‌شود که هر کدام دارای محدودیت‌هایی مانند راندمان کم و یا هزینه بالا هستند. استفاده از فناوری نانو یکی از راهکارهایی است که اخیراً مورد توجه قرار گرفته است. این روش با کاهش ابعاد مواد به نانومتر، عملکرد را بهبود می‌بخشد. انواع مختلفی از نانومواد وجود دارد که به دلیل خواص منحصر به فرد خود مانند سطح تماس بزرگ‌تر، توانایی کار در غلظت‌های پایین و غیره، پتانسیل بالایی برای تصفیه مؤثر آب‌های آلوده دارند. مطالعات نشان می‌دهد که می‌توان از آن‌ها در اشکال مختلف مانند نانوجاذب‌ها، نانوغشاها، نانوفیلترها و نانوفوتوکاتالیست‌ها برای حذف یا کاهش آلاینده‌ها به‌ویژه از پساب نفت، گاز و پتروشیمی استفاده کرد. در این بررسی به اهمیت و کاربرد فناوری نانو در تصفیه پساب نفت، گاز و پتروشیمی می‌پردازیم.

واژگان کلیدی: فناوری نانو، صنایع نفت و گاز، تصفیه پساب، نانوغشا، نانوجاذب، نانوفوتوکاتالیست

بررسی اثر شوری آب بر روی رسوب آسفالتین به کمک معادله‌ی حالت PC-SAFT

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چکیده

رسوب آسفالتین در فرآیندهای تزریق آب کم‌شور در دهه‌ی اخیر توجه بسیاری داشته است. در این مطالعه برای بررسی تاثیر شوری آب بر روی رسوب آسفالتین از معادلات ePC-SAFT استفاده شده است. در این راستا، برای پیشبینی رسوب آسفالتین از یک مدل جامد با نفت مدل شامل هپتان و تلوئن با نسبت ۷۰ به ۳۰ استفاده شده است. با هدف کمینه سازی تابع هدف AAD بین داده‌های آزمایشگاهی و داده‌های بدست آمده از مدل در الگوریتم بهینه‌سازی ازدیاد ذرات از سه پارامتر قابل تنظیم استفاده شد. نقش شیمی آب در رسوب آسفالتین با تغییر ترکیب آب دریا (SW) از طریق تنظیم قدرت یونی با یون‌های دو ظرفیتی مورد بررسی قرار گرفت. برای درک بهتری از نقش یون‌های دو ظرفیتی (Mg^{2+} ، Ca^{2+} و SO_4^{2-})، سه آب نمک ساختگی شامل نمک‌های $MgCl_2$ ، $CaCl_2$ و Na_2SO_4 مورد استفاده قرار گرفت. نتایج نشان می‌دهد که در شوری‌های پایین نمک‌ها (۵۰۰۰ ppm) مولکول‌های آسفالتین به سمت سطح تماس آب/نفت مهاجرت می‌کنند که منجر به کاهش رسوب آسفالتین می‌شود. بعد از این غلظت به سبب شکستن پیوند بین آسفالتین- یون رسوب آسفالتین کاهش پیدا می‌کند. طبق نتایج، میزان رسوب آسفالتین پایین‌تری برای آب دریای رقیق شده (۲ و ۱۰ بار رقیق شده) مشاهده شد که می‌تواند از نظر انبساط لایه‌ی الکتریکی دوگانه تشکیل شده مورد بحث قرار گیرد. نتایج مقایسه بین داده‌های آزمایشگاهی و مدل نشان می‌دهد که مدل پیشنهادی قادر به پیش‌بینی رسوب آسفالتین برای آب نمک‌های $MgCl_2$ ، $CaCl_2$ و Na_2SO_4 با خطای نسبی مطلق کمتر از ۷٫۶۸ درصد، ۵٫۴۴ درصد و ۸٫۳۹ درصد است. یافته‌های حاصل از این مطالعه اهمیت طراحی یک فرآیند تزریق آب کم‌شوری کاربردی را روشن می‌سازد.

واژگان کلیدی: مدل جامد، رسوب آسفالتین، معادله حالت ePC-SAFT، تزریق آب کم‌شور

استراتژی انتخاب مواد برای کنترل خوردگی در صنایع بالادستی نفت و گاز ایران

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چکیده

سالانه مبالغ بالایی به خاطر مشکلات ناشی از وقوع خوردگی در صنایع بالادستی و پایین دستی نفت و گاز، از دست می‌رود. به منظور کنترل هزینه‌های خوردگی، اخیراً مفاهیم کنترل خوردگی و مدیریت خوردگی توسعه یافته‌اند. هدف از فلسفه مدیریت خوردگی کاهش هزینه‌های خوردگی و افزایش ایمنی با فرآیند ارزیابی مجدد در مراحل مختلف پروژه است. فرآیند انتخاب مواد یکی از مراحل کلیدی در تضمین یکپارچگی سیستم بوده و نقش مهمی در سیستم جامع کنترل خوردگی ایفا می‌کند. برخی از پارامترهای مهم در انتخاب مواد مناسب برای کاربردهای مختلف شامل: فشار و دمای طراحی، جوش‌پذیری، مسائل مالی و سایر ملاحظات خوردگی می‌باشند. استانداردهایی مانند ISO 21457 تهیه سند رویه انتخاب مواد قبل از مراحل اجرایی پروژه را الزامی نموده است. بدون داشتن رویه‌ای مشخص برای انتخاب مواد، فرآیند انتخاب مواد به دلیل تنوع در کدها و شرایط سیال سرویس، کاری بسیار پیچیده و گیج‌کننده به شمار می‌آید. هدف از این مطالعه ارائه خلاصه فرآیندها و رویه‌های مرسوم در شرکت‌های بالادستی نفت و گاز برای انتخاب مواد در شرایط وجود خوردگی در نتیجه CO_2 ، H_2S و نمک می‌باشد. همچنین تدابیری برای رفع معضل آلودگی محیط‌زیست در نتیجه نشت فرآورده‌های هیدروکربنی به محیط‌زیست با رویکرد انتخاب صحیح مواد مورد بحث قرار گرفته است.

واژگان کلیدی: انتخاب مواد، خوردگی، صنعت نفت و گاز، مدیریت خوردگی

شبیه‌سازی انفجار خط لوله گاز طبیعی به کمک نرم‌افزار PHAST و تأثیر شیرهای خودکار بین‌راهی

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چکیده

در ایران برای احداث بنا در کنار خط لوله گاز همواره بایستی دو مسئله مورد بررسی و رعایت قرار گیرد اول میزان تراکم ابنیه و دوم فاصله از محور خط لوله گاز و این دو مورد توسط جداول استاندارد IGS-C-SF-015 تعیین می‌گردد. این در حالی است که این معیارها به‌تنهایی نمی‌توانند میزان ریسک موجود را تعیین کنند. برای این منظور بهترین راهکار استفاده از محاسبات یک نرم‌افزار معتبر مانند PHAST می‌باشد. این نرم‌افزار علی‌رغم قدرت بالای محاسبات پیامد خطر همواره برای ارائه پاسخ منطقی نیازمند ملاحظات می‌باشد. مثلاً این نرم‌افزار به‌تنهایی قادر به محاسبه اثرات خاک روی لوله نمی‌باشد و یا تأثیر برخی از وسایل مانند شیرهای اتوماتیک را نمی‌تواند به‌تنهایی و بدون تحلیل کاربر لحاظ نماید. در این مقاله سعی می‌شود با مدل‌سازی یک خط لوله غیر مدفون در خاک که به‌صورت حقیقی دچار انفجار گردیده مبنایی برای یک مدل منطقی تعیین شود پس از آن می‌توان اثر یک سیستم قطع اتوماتیک خط موسوم به LBV را (که در ایران برای حفاظت تمامی خطوط لوله گاز فشارقوی استفاده می‌شود) برای نخستین بار با یک دقت عملی تعیین نمود. به این صورت که پس از به دست آوردن مدل شبیه‌سازی شده انفجار واقعی، ابتدا شرایط خط را با توجه به نرخ افت فشار ایجاد شده برای عملکرد صحیح LBV بررسی نموده و پس از آن به کمک نمودار پیامدهای انفجار در دو حالت عملکرد LBV و عمل نکردن LBV مورد مقایسه قرار می‌گیرد. برای حالت حادثه شده می‌توان نتیجه گرفت که عملکرد صحیح این سیستم حفاظتی تا میزان بیش از ۶۰ درصد می‌توانسته از مساحت تحت تأثیر حادثه را کم نماید.

واژگان کلیدی: خطوط لوله گاز، PHAST، شیر خودکار، پیامد



JOURNAL OF GAS TECHNOLOGY

VOLUME 7 • ISSUE 1 • SUMMER 2021

EISSN: 2588-5596

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