Study on Chemical Cleaning Agent in Treatment of Abandoned Oil Pipeline

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Abstract. After pipeline construction burst china energy pipeline industry commonly faced with aging and abandonment problem. The study on pipeline abandonment was still in preliminary state, because there is nearly no pipeline abandonment standards and guidelines. Pipeline cleaning is the first step to dispose the abandoned pipeline to eliminate the risk of environment and safety. In foreign developed countries there are many chemical cleaning agents. But this chemical cleaning agent is not suitable for residual of chinese pipeline because of oil difference between china and foreign country. The most of residual in china have a very high paraffin and resin-asphaltenes content. So preparation of chemical cleaning suitable for china residual is a challenge on the technology of abandonment pipeline. In this paper two kinds of chemical cleaning agent were prepared to clean the different type of residual. They are hydrophilic chemical cleaning agent and oil soluble chemical cleaning agent. The result of cleaning project shows that the both kind of chemical cleaning have good performance for the abandoned pipeline. The chemical cleaning agents will assist pipeline company to totally clean the abandoned pipeline to ensure the public safety and environment protection.

1 Introduction

The oil pipeline in china has been increasing for the past several decades, and these pipeline includes the pipelines occupied by Petrochina, Sinpec, Cnooc and other company in china. The all of oil pipeline in china exceeds ten thousand kilometres by now\cite{1}. This pipeline infrastructure is fundamental to the efficient, safe and reliable delivery crude oil or refinery oil from overseas to domestic markets, from oil fields to refinery factory or customers. But with the time prolongs, some of the pipeline have to be abandoned because the oil field has stepped into its last period and the oil in these oil field is almost been drying up. One typical example is Daqing oil field. Several pipelines from oil field to refinery factory are abandoned because crude oil output of Daqing oil field become lower and lower. The abandoned oil pipeline in the northeast of china has exceed 3000 kilometres.

Since the promulgation of Oil and Gas Pipeline Protection Law of the China in 2010, associated laws were newly modified or developed, including Environmental Protection Law of the People’s Republic of China, Water protection Law of the People’s Republic of China, and soil Protection Law of the People’s Republic of China have been successively promulgated. China gets more focus on environmental issue of abandoned pipeline. The first China industry standard on abandoned pipeline is applied for in 2015, named technical specifications for the disposal of an abandoned oil and gas long distance pipeline. The standard on abandoned pipeline (SY/T 7413-2018) is released and implemented on the April 1st 2019. The abandoned pipeline is must be cleaned to meet the requirement of the standard (SY/T 7413-2018) and there is no wax, no oil on the inner surface of the pipeline.

It is well known that many technologies of treatment on abandoned pipeline were firstly developed in the United states, Canada, Netherland, Russia etc. Cleaning technology includes the following technologies\cite{2}, but not limited to:

- Residual cleaning
- Grouting
- Plugging
- Removing
- Waste treatment

Cleaning the residuals in the pipeline is the first step to dispose the abandoned pipeline. After cleaning residual the pipeline will be abandoned in place or removed. The cleaning procedure is mandatory step to disposal the abandoned pipeline to eliminate the risk of environment and safety.

There are many cleaning methods to clean oil pipeline. These cleaning methods are classified two kind of type, one is mechanical cleaning method, and the other is chemical cleaning method. Compared with the mechanical cleaning method, chemical cleaning have the advantages bellow\cite{3}.
Instant achieving of safe conditions for flame cutting and welding (no flammable vapors in the pipeline) improves safety
reduces time and costs of dismantling work
No risk of environment pollution during dismantling and modification work
No risk of environment pollution in case the pipeline remains conserved for a future use or abandoned in the earth.

Comparing two kind of cleaning method, it is well known that chemical cleaning method is more economical and simple. This is conclude by study on abandonment pipeline that was conducted by pipeline company of petrochina from 2014. Studies have shown that significant quantities of contaminants will be left in abandoned pipelines as a result of poor cleaning operation. The following factors will influence the affection of cleaning operation[4].
- Pipeline configuration (e.g. bends and doglegs)
- Type and quantity of chemical cleaning agent
- choose of pig and its proper pig use
- Diameter of pig
- Chemical cleaning operation procedure

If an abandoned pipeline is piggable, chemical cleaning could be started. Usually, chemical cleaning procedure includes the following steps:
- Pipeline dividing to cleaning sections
- Local modifications,
- Installation of temporary pig traps,
- Calculation of needed contact time and volume of chemical cleaning agents,
- Composition of cleaning pig trains (number of pigs), volume and content of cleaning batches and pig train travel speed,
- Delivery of suitable pigs, chemical agents, pumps, air compressors, nitrogen units etc.
- Disposal of waste.

The whole cleaning procedure and waste disposal should be described in a detailed engineering study. Pipeline should be cleaned by pigging as well as possible prior to other pipeline abandoned disposal.

Usually, there are two types of cleaning agents they could be selected. They are hydrophobic cleaning agents (oil soluble) and hydrophilic agents (water soluble)[5]. Oil soluble cleaning agents are mainly used to improve the efficiency of pipeline cleaning process to remove paraffins and dissolve hard paraffin deposits from internal pipeline wall. Water soluble cleaning agents can very efficiently remove rests of oil from internal pipeline surface. Choice of chemical agents are based on
- Composition of crude oil,
- Content and nature of deposits - paraffin, hard deposits, black powder,
- Pigging history.

Choice of suitable cleaning agents is very important for the job. It usually depends on the laboratory experiment. In this paper, two type of cleaning agents was prepared and its performance was tested.

### 2 Preparation of Chemical Cleaning Agent

#### 2.1 Preparation of Cleaning Agent

Several substances are used in order to prepare chemical cleaning agent. They are including penetrating agent, wax solvent, co-solvent, surfactant, emulsifying agent, dispersant etc. when chemical agent contact with residual on the inner surface of the pipeline, the penetrating agent will penetrate into the bottom side of the wax on the inner surface of the pipeline. Then, residual will drop off from the surface of the pipeline. The piece of residual dropped from the pipeline surface will resolve in the solvent and co-solvent. Dispersant of the chemical agent will dispersant the residual into the solvent. The emulsifying agent will improve the dissolving capacity of the solvent.

The chemical agent is prepared use the following mixing equipment. The mixing equipment is show by Fig.1. To the penetrant, wax solvent, co-solvent, surfactant, emulsifying agent, dispersant were added to the cup in suitable sequence and mixed for a period of time. The speed of the mixing equipment can be adjusted.

#### 2.2 Performance Test

##### 2.2.1 Dissolving speed

Dissolving speed of the chemical cleaning agent is test in the circle loop equipment. Dissolving speed is calculated by the following formula (1).

\[ V = \frac{h}{t} \]  

Where, \( V \) is Dissolving speed, mm/min
\( h \) is the average thickness of residual in the inner surface of pipeline, mm
\( t \) is the dissolving time, mm

##### 2.2.2 Dissolving capacity

Dissolving capacity of the chemical cleaning agent is tested by equipment shown in the Fig.2. Dissolving capacity is calculated by the following formula (2).

\[ Dc = \frac{m}{m_1} \times 100 \]  

Where, \( Dc \) is dissolving capacity of the chemical cleaning agent, g/100g
\( m \) is the maximum weight of residual that 100g chemical cleaning agent can dissolve
\( m_1 \) is the weight of chemical cleaning agent.
It can be seen that there is a blender attached to the dissolving capacity test equipment. The blender is used to mix the system to imitate the turbulent flow when chemical cleaning agent flows in the pipeline. When testing the dissolving capacity the mixing speed should be as low as possible because the chemical cleaning agent flows very slowly in the pipeline.

3 Results and Discussion

3.1 Hydrophilic Chemical Cleaning Agent

Hydrophilic chemical cleaning agent is a kind of water soluble agent. The recipe includes including penetrating agent, wax solvent, co-solvent, surfactant, emulsifying agent, dispersant and water. The choice of solvent, co-solvent, surfactant, emulsifying agent, dispersant type is very important for the cleaning performance. Organic solvent have high dissolving speed for wax is usually chosen as solvent and co-solvent, such as toluene, benzene, gasoline, diesel fuel etc. the type of solvent and co-solvent have remarkably effect on the dissolving speed of the chemical cleaning agent. Toxic substance is forbidden to add into the chemical cleaning agent, because toxic substance is harmful for human being health and environment. If it is leaked into the environment, it will destroy ecological environment. Penetrating agent is a compound with small molecular weight the can easily penetrate into the bottom side of the wax on the inner surface of the pipeline.

Surfactant is substance that can easily reduce the surface tension of the solid-liquid, liquid-liquid surface. The ordinarily nonionic, anionic and cationic surfactant could be used in the chemical cleaning agent. This kind of substance can increase the dissolving capacity of the chemical cleaning agent. Furthermore, it also can increase dissolving speed of chemical cleaning agent. When penetrating agent penetrates into the bottom of the residual, a little piece of residue will drop of from the pipeline. At this time, dispersant will disperse the little of residue into the chemical cleaning and become smaller piece or stable suspend liquid. Emulsifying agent is very useful to make the system more stable. It is important to the cleaning performance and storage stability.

The substance in the recipe is mixed with a blender at the mixing speed of 600r/min. the chemical cleaning was prepared and it shows a kind of white emulsion just like a milk. This kind of chemical cleaning agent is very stable at period of translation and storage. 10tons chemical cleaning agent was prepared using the laboratory recipe of the tabl. This chemical cleaning agent was used to clean oil pipeline of northeast china. One kilometre pipeline selected from abandoned pipeline about 300 kilometres in order to test the performance of the chemical cleaning agent. Thickness of the residual is about 150-200 mm. It can be seen from a picture of the Figure 3. Firstly, the one kilometre pipe was divided from the abandoned pipeline. It was not pigged in the past, but integrity of the pipeline is good. It can hold with the pressure needed for the pigging process. The pipeline is respectively pigged by pathfinder ball, polyurethane pig, straight plate pig and paraffin crapper pig once time or more. Residual was collected and analysed. The analysis result shows that residual is dominated by paraffin and resin-asphaltene. Firstly, the dissolving speed was test in the laboratory. The result shows that the chemical cleaning agent can remove residual from the inner surface in a short time under normal temperature. And then a detail cleaning plan was made according to the laboratory result. After ten days cleaning of pig train, the effect of cleaned inner surface is showed in the b picture of Fig.2.

| Num. | Substance     | Content (wt%) |
|------|--------------|--------------|
| 1    | diesel fuel  | 15           |
| 2    | acetone      | 8            |
| 3    | n-hexane     | 6            |
| 4    | SDBS         | 2            |
| 5    | AS-40        | 0.8          |
| 6    | UDA-50       | 1.0          |
| 7    | water        | 67.2         |

The optimized recipe was shown in the table1.

![Effect of hydrophilic chemical cleaning agent](image)

**Fig.2.** dissolveing capacity test equipment for preparation of chemical cleaning agent

**Fig.3.** Effect of hydrophilic chemical cleaning
From the figure, it can be seen that good cleaning effect was obtained. The cleaned pipeline meets the requirement of pipeline company and local government. Because the pipeline is closed to the building of resident, it was abandoned in place.

3.2 Hydrophobic Chemical Cleaning agents

In some cases some pipelines were out of service for a long time. A short section was cut from the long abandoned pipeline. It was found that the residual was hard because the substance with a low boiling point had volatilized. It was found that the cleaning performance of hydrophilic chemical cleaning agent is not good for the aged residual. In order to solve this problem, hydrophobic agent was developed. The hydrophobic agent is a kind of oil soluble agent. It is mixture of organic compound. According to the ingredient of the aged residual the oil soluble agent was studied. Various organic compounds were used to optimize the performance of the oil soluble chemical cleaning agent. The optimized recipe was shown in the table 2.

Table 2. Substance list of the oil soluble recipe

| Num. | substance                      | Content (wt%) |
|------|-------------------------------|---------------|
| 1    | dimethylbenzene                | 45            |
| 2    | n-hexane                      | 40            |
| 3    | ethylene glycol monomethyl ether | 10         |
| 4    | SDBS                           | 5             |

The substance in the recipe is mixed with a blender at the mixing speed of 300r/min. the oil soluble chemical cleaning transparent liquid. In order to test the performance of oil soluble chemical cleaning agent for the aged residual, about two kilometre pipeline was divided from the pipeline that has been out of service more than three decades. Thickness of the residual is about 10 mm. the sample of the residual is very hard. The residual is peeled from the pipeline and analysed. The analysis result shows that residual is composed of wax, mechanical impurity and sandy particulate. It could be indistinctly seen from the Fig.4. In this time, the cleaning procedure is different from that of pipeline with thick residual. Fortunately the pipeline’s integrity is also very good because the cationic protection system is in the operation. In the former example, the first step is not used in this case because the inner residual is too hard to make the pig block. The oil soluble chemical cleaning agent with one pig separately at both the head and end of liquid cylinder was injected into the abandoned pipeline. At some cases some amount of extra oil soluble chemical cleaning agent could be inject before the first pig to avoid the pig blocking. The cleaning effect of the pipeline for aged residual can be seen from a picture of the Fig.5.

4 Conclusions

Pipeline cleaning is the first step to dispose the abandoned pipeline to eliminate the risk of environment and safety. Two kinds of chemical cleaning agent were prepared to clean the different type of residual. They are hydrophilic chemical cleaning agent and oil soluble chemical cleaning agent. The result of cleaning project shows that the both kind of chemical cleaning have good performance for the abandoned pipeline.

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