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HYDRATES, - THE START OF A CHAIN REACTION LEADING TO THE PIPER ALPHA DISASTER?

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At a certain time point, Cremer & Warner, the technical adviser to the Inquiry, had constructed several possible scenarios linking hydrates to process upsets or hydrocarbon leakage.

PETRECO evaluated these scenarios and performed relevant laboratory tests to minimize the number of likely scenarios and produce more detailed insight into the physical behaviour of hydrates in a few of the scenarios.

SUMMARY

From evidence given by survivors of the Piper Alpha disaster as well as the technical evidence collected or produced during the following public inquiry, it is very possible that Hydrates played a major role as an initiator of the Disaster.

Hydrates, in this context, means a solid substance formed by water and light hydrocarbon molecules at elevated pressures and temperatures well above normal freezing conditions for water.

Hydrates in general pose a threat to hydrocarbon process systems due to the fact that they are solid materials within systems essentially designed for fluids.

On Piper Alpha they had just a few days ahead of the disaster, altered the normal process to perform maintenance on equipment for removing water from the produced condensate stream. This would imply that there was a good possibility of hydrate formation within certain parts of the process. Subsequently there were actions taken to prevent this formation by injection of considerable quantities of hydrate inhibitor, e.g. Methanol. Certain parts of the evidence however, suggests that the amount of inhibitor not was sufficient for extended periods of time.

To investigate the behaviour of process fluids under physical conditions as given in evidence, a series of physical laboratory simulations were performed by PETRECO. These involved forming and observing hydrates in a test facility using correctly composed fluids as well as actual process conditions such as temperature, pressure and flow.

A number of different scenarios linking hydrates to a hydrocarbon leakage were examined and judged on the basis of calculations and observations of mechanical properties of hydrates possibly formed within the Piper Alpha process.

Based on the results of this work a series of events were postulated that indicates a mechanism for the tripping of condensate pump B.

INTRODUCTION

The assignment to perform the work in part presented herein was given to PETRECO on 7th August 1989 by Cremer & Warner.

From evidence supplied to the Inquiry at the time of commissioning the work, it was not certain whether, had hydrates occurred, they would have been a problem and could have led to a possible cause of the initial leak. The requirement was therefore to review various points on the plant where hydrates might have formed or accumulated and to discuss whether any such problem could give rise to a leak, utilizing experimental test results if necessary.

The basis of information necessary to perform this work was presented in the form of relevant previous reports, notes, drawings and evidence given by survivors of the disaster.

Using this information it was possible to identify the most likely locations in the process where hydrates would have formed.

This formed the groundwork from which relevant tests could be devised thus enabling refinement of initial findings and conclusions based on the experience from years of hydrate properties testing in the PETRECO laboratories.

PROPERTIES OF HYDRATES.

Hydrates are formed as a solid material from liquid water and different molecules of a size enabling them to fit into the lattice formed by water molecules tied together by hydrogen bonds. The presence of this molecule stabilizes the water structure and turns it into a solid material at temperatures well above normal freezing conditions. The molecules are normally of a size of Butane molecules or less. Examples of hydrate forming molecules are: Methane, Ethane, Propane, Isobutane, Carbon dioxide, Hydrogen sulphide, Nitrogen. There are many other hydrate formers as well, not normally present in hydrocarbon streams.

As a result of the low solubility of most natural gases in water, the actual hydrate forming process takes time. If water and gas is left standing still the process may take weeks. The presence of other non hydrate forming hydrocarbons will slow down the process since they tend to prevent direct contact between the water and the hydrate forming molecules.

A system with hydrate forming gases or liquids only, plus water, can result in an instantaneous reaction once the conditions are met. A close to ideal situation for hydrate forming is obtained if water is sprayed into a gaseous atmosphere where the pressure and temperature are within the hydrate region.

This is due to the large contact area between water and gas for diffusion of gas into the water structure, as well as the low diffusion resistance. As known, this is the typical situation down stream of an expansion choke.

Hydrates may develop mechanical properties long before a stoichiometric equilibrium has been reached between water and gas molecules.

In a liquid system, the first hydrates normally appear in the water phase as tiny grains and will then grow to produce a slushy substance.

Whether or not this substance is harmful to the process depends upon the dispersion abilities of the liquid HC-phase. This, is in turn dependant upon the content of naturally occurring surface active elements in the liquid hydrocarbon as well as the flow velocity.

In light condensate streams with velocities of less than 1 m/s, the water is hardly dispersed at all. It moves along the bottom of horizontal pipes and may also gather in pools at low spots of the system or ahead of upwards pointing bends.

As stated earlier, hydrates formed in hydrocarbon streams with little or no pipe wetting or water dispersing capabilities, present the most problems. They are capable of sticking to the smoothest surface and most certainly in and on any mechanical obstruction like; welded joints, pipe seams, pipe tappings, branches, bends or valves.

From observations made by PETRECO, hydrate plugs are formed in two ways. The first process involves sticky hydrates adhering to the wall thereby providing an anchor for later arriving masses of hydrates. Normally the first hydrates are not very solid, nor do they have a high degree of integrity. However, if packed mechanically, they can easily turn into an ice-like structure. This is likely to occur shortly before plugging when the layer of hydrates on the pipewall has grown enough to be subjected to considerable drag from the hydrocarbons still flowing.

Another mechanism for plugging can be observed if the hydrocarbon system does not produce sticky hydrates. A soft plug of hydrates can then be transported along the stream covering maybe 10% of the cross sectional area of the pipe. Upon hitting a mechanical obstruction, the hydrate "train" will start compacting and piling up. Within a few seconds a plug could be formed.

It is also possible for the hydrates to stick on the pipe walls for some time, thereafter loosening upon a slight temperature increase, and form a soft travelling plug. This may upon hitting an obstruction, form a hard plug and block the pipe.

Of vital importance, is the fact that hydrates can be formed in one location of a process system whereas the problems, might be observed at another point.

It has been observed to take quite a lot of heat and therefore time, to dissolve hydrates once they are formed. Hydrates that are formed may therefore survive as solid materials after being transported into areas of a process with pressure and temperature conditions well outside the hydrate region.

If the pressure is released, down stream of a hydrate plug, the plug will release gas at that end, and turn into hard ice. This process cools the hydrates/ice down considerably and it will in some cases also lead to a bulk expansion of the plug.

A hydrate plug of 50 kilos trapped and released by adding heat to a pipe holding back 40 - 100 bars pressure, will upon release be subjected to an acceleration of 50 to 150 times that of gravity, i.e. like a rifle bullet. This may of course lead to pipe rupture. Applying heat to a hydrate plug, or letting it warm while still under pressure at one end only, is thus not good practice.

If a hydrate plug is formed in a pipe line it will usually be shaped and hardened by the differential pressure across it. If additional pressure is applied it may be released upon exceeding the shear strength of the plug or its grip to the pipe wall. Such a plug will of course be accelerated in a similar manner to a heated plug under pressure.

Some of the hypothetical leak scenarios involving hydrates, suggested a plug release followed by pipe rupture.

EVALUATION OF POSSIBLE HYDRATE PROBLEMS AT DIFFERENT LOCATIONS OF THE PIPER ALPHA PROCESS.

By the time PETRECO was hired, a number of reports and statements had been made on the subject of hydrate formation conditions, and given as evidence to the court. This work was reviewed by PETRECO and found to be consistent with engineering practise around the world.

The conclusion was that provided all information given regarding pressure, temperature and composition of the process streams were correct, and that the methanol injection rates were as reported by Occidental representatives, no hydrates should have been forming on Piper Alpha on the 6th of July 1988.

There was however, evidence from production logs, statements etc. that suggested that the methanol injection was not kept at the full injection rate all the time and that the temperatures over extended periods were somewhat different from those reported. Accordingly the process had to be examined with a view to investigating the effects of these process changes.

Earlier in the Piper Alpha Inquiry, a number of locations had been identified as offering sites for potential hydrate formation. Such factors as presence of free water, degree of cooling, presence or absence of methanol and likely mechanical properties were all considered in formulating a judgement for these locations. The judgement was initially based on experience but was latterly revised as necessary as test data became available.

The conclusion after reviewing the different scenarios was that only a few of them were likely or possible. All of the plug release/pipe rupture scenarios were ruled out for different reasons.

The effects of certain well defined process upsets were also considered and are summarized here.

a) Possible Low Centrifugal Compressor Discharge Scrubber Temperature

The effect of a lower Centrifugal Discharge Scrubber Temperature would be that more water would condensate at the scrubber rather than at the J-T drum. This might have an impact on the hydrate inhibitor concentration at different locations of the process. Evidence, brought forward during the study showed however that the temperature most probably was not low and this possibility was ruled out.

b) Mal operation of the manual drain down procedure from C-202.

The water in this vessel was usually drained down manually every second hr. However, if this was omitted, an overflow of water would go to the J-T drum and add to the amount of water requiring hydrate inhibitor. Due to the size of this vessel, the flowrate of water into it and the relative amount of this water compared to what was already condensed at the J-T drum, the conclusion was that this would not have made a significant change in the situation provided the methanol injection was at its intended rate.

c) Methanol supply failure

Methanol supply failure to the J-T flashdrum could be of utmost importance. From the given evidence it was shown that the pump head supplying methanol upstream of the J-T drum, was probably out of service for 4 hrs on the 6th of July.

Furthermore, from other pieces of evidence, the same methanol pump head, had been out of service for some 15 to 20 minutes on 5th July in order to stop a packing leak. On both occasions this would have resulted in a loss of 18.0 US gph of methanol upstream of the J-T valve. Thereby reducing the methanol concentration immediately downstream of the valve from 25 % to 14 % by weight.

Accordingly the potential for hydrates to form at the J-T valve and accumulate downstream in the condensate system required to be examined more closely.

d) Possible Low temperature in the J-T flashdrum

Low temperature in the J-T flashdrum is highly interconnected with the tendency to form hydrates. From the fiscal metering log sheet of July 5th it was seen that the temperature of the condensate metered downstream of the condensate injection pumps, was about 12-13°C (53-56°F). The J-T flashdrum would normally be about 2-3°C colder than this, as the condensate was heated upon passing through the condensate pump.

Hence it is very likely that the J-T flashdrum was operating at around 10°C (50°F) on 6th of July. Experiments and calculations have shown that this temperature would probably be in the critical range if the methanol concentration was reduced to around 15% by weight. It was therefore important to examine the effects of a 4 hour reduction in methanol supply and the low temperature in the J-T Drum further in the light of the test findings.

TEST PROGRAM, PHILOSOPHY AND RESULTS

The different scenarios involving hydrates could be grouped into a few standard cases involving slightly different mechanisms for the hydrate plugging itself. Some of them involved assumptions of leakage in valves or malpractice in operations.

The cases selected for testing were those representing the cases having the higher possibility in the previously mentioned list of scenarios involving hydrates. These were:

- i) Gradual hydrate formation in flowing wet condensate. Plugging by sticky hydrates, overpressurization of pipework.
- ii) Process flow cooled down by J-T mechanism, the combination of free water and cooling leading to plugging by ice or hydrates (i.e. similar to cases a) and b) above) but causing overstressing of pipework.

The tests were planned and executed using a realistic fluid composition, pressures, temperatures and a range of methanol content, based on previous evidence.

All the tests were performed on and within the PETRECO wheel shaped flow simulator shown in fig. 1.

Every time a test was prepared, the wheel was filled with a mixture of gases and liquids leading to the correct composition. The gases were added one by one from gas bottles starting with n-butane and ending with methane. Finally, n-pentane, iso-pentane and hexane was injected in liquid form.

No iso-butane was available and this gas therefore was omitted from the gas mixture. (Based on the excellent agreement between experiment and calculated, values for hydrate formation this omission did not have a significant effect).

This procedure produced a wheel filled with around 0.5 litres of condensate and the rest, about 8 litres of gas at around 42-43 bar and 7°C.

Some Reference tests were performed after adding some water to the hydrocarbon mixture and the wheel was thereupon set in rotation. The rotation used, gave a flow velocity of 0.5 m/s during a temperature decline and rise within a period of 1000 minutes (17 hrs). The velocity was chosen to get some mixing of water and hydrocarbons and to see if the hydrates would stick to the pipewalls. It was also close to the actual velocity in the condensate lines.

During the injection-tests, the water was kept outside the wheel while the wheel was rotated at 0.5 m/s to condition the hydrocarbons at the right temperature. The water was then cooled down to this temperature and injected into the gas phase and above the condensate in the wheel, while the wheel was stationary.

A water spray was obtained by injecting through a spring loaded non return valve at 20 bar above wheel pressure. Normally the injected volume of water would be 2-300 ml. This injection procedure simulated the conditions down stream of the J-T valve quite well, although in the real case the water would already have had a certain amount of hydrate forming molecules in solution. In addition, its velocity would have been much higher. This probably resulted in slightly slower hydrate reaction rates in the experiments than in the real case.

CONCLUSIONS DRAWN AFTER TESTING OF HYDRATE PROPERTIES.

The point in the phase 1 operating process having the greatest hydrate potential was undoubtedly, just downstream of the J-T valve where rapid cooling took place, and in the J-T flashdrum. If the formation of hydrates was not initiated at or before the J-T flashdrum they were not likely to have been converted within the condensate system. Hydrates formed, either as a result of gradual cooling in a condensate line, or at the J-T valve, containing no methanol, could have been very sticky. They would have most certainly stuck to all metal surfaces upon contact.

However, on increasing the methanol content ahead of formation, this stickiness deminished and with it, also the firmness of the hydrate masses. Therefore in the situation where hydrates were formed at the J-T valve and some methanol was present, a mobile hydrate slurry would have been formed.

It could also be said that around 10°C, the water entering the J-T flashdrum would convert to hydrates instantaneously if no methanol was added. Even if an amount of 15% by weight had been added, a large portion would rapidly convert to hydrates while the rest would remain as water. Some of this water might convert again to a hydrate slurry downstream, if trapped in pools for some time. (0.5 - 1hr).

Hydrates, formed at say 7°C may well have survived with mechanical properties intact for several hrs at 11-12°C.

It could therefore be concluded that any hydrates appearing in the line from the J-T valve to the main oil line most likely would have been formed at the J-T valve itself.

Pressurising the flow through the condensate injection pump would not necessarily increase the hydrate potential due to the combination of pressure- and temperature increase. In some cases more methanol might be required to prevent hydrates at the pump, whereas in some cases it might not. This would depend on the working conditions of the pump as well as the methanol concentration at that point.

Physical simulation of the combined pressurisation and agitation within the condensate injection pump is quite difficult without having a similar pump system. Hence, it is possible that the tests at this point underestimated the hydrate potential of the pump.

However, it can be stated that if a concentrated mixture of water and hydrates was pumped through, rather than hydrocarbons, the rise in temperature would be quite low. (Less than 0.1°C, 0.2°F compared to the 2.4°C (4.3°F) reported for hydrocarbons). This, in combination with the pressure increase (see fig. 2) would be likely to increase the hydrate potential considerably. The implication from this is that a mixture of mostly water phase could be pushed far into the hydrate region when passing through the condy pump, whereas a mixture of mostly hydrocarbons would not.

It was shown that the calculated values for hydrate formation were in good agreement with experiment. However, the calculations will produce the hydrate melting point and not the actual formation point. In experiments, this formation was measured to take place up to 12°C lower than the calculated melting point, when exposing the water/ HC-system to a gradual cooldown. The implication of this is that the gradual process of hydrate formation upon cooling into the hydrate region, was very inhibited. In the condensate pipework this meant that formation would normally not have taken place unless the temperature was reduced to at least 6°C, and then only without methanol injection. This is highly unlikely even after taking into consideration the measurement accuracy on Piper Alpha.

These conclusions confirmed that hydrate formation due to rapid cooling at the J-T valve was the most likely cause of hydrates on Piper Alpha. This scenario is therefore discussed further in the next section.

SUGGESTED HYDRATE SCENARIO LEADING UP TO TRIPPING OF CONDENSATE PUMP B.

When considering the possible consequences of hydrate formation it was necessary to consider also the nature of the flow and distribution of water at various parts of the condensate system.

The relatively small flow of liquid compared to gas upstream of the J-T valve would not have caused fluctuating flows and hence variations in water content. Hence it is unlikely that hydrates would have formed due to uneven dosage of methanol into the aqueous stream at this point. Eventual hydrates that were formed must therefore have been formed during periods of less than adequate methanol injection.

The streams between the J-T flashdrum and the main oil line carried condensate and water at an average velocity 0.5 m/s. This velocity was sufficiently low for stagnant water accumulation to have occurred within the pipe.

If hydrates, in the form of a slurry, were carried forward into such pools of water after forming at the J-T valve, they would have changed this picture. A hydrate slurry would not have been easily broken into individual droplets like water, hence the level of water/ hydrate would have changed. Since water would have been transported out more easily, the hydrates might have accumulated in the pipes for some time, whereas the water would have been transported through.

Since the J-T flashdrum did not have an upstand at the condensate outlet, there was no stable water level inside it. (The production of water would be only 0.13 m³ litres of water per hr. compared to the condensate production of nearly 50 m³ litres per hr). Without a water layer, the hydrates would be able to contact the steel bottom of the vessel and build up around a central channel flow of water to the outlet of the flashdrum.

The hydrate buildup would occur at the bottom of the vessel along its main axis which would not have favoured gravity drainage of the slurry. The velocity of the condensate inside such a vessel would have been of the order of a few cm/sec. and would have produced insufficient drag on the hydrate slurry to make it flow to the outlet.

Evidence indicated that there was a loss of methanol to the J-T valve on the 5th (15-20 minutes) and 6th (4 hours).

Whilst tests indicated that hydrates would have been likely to form during both periods, it was thought that those formed on the 5th would not have been sufficient (less than 50 kilos) to have caused any process problems.

It is likely that they accumulated in horizontal sections of the pipework during this period and either remained there dissolving slowly in the increased methanol concentration after restart of the pump head, or were mobilised and gradually carried harmlessly forward.

However, if a similar situation existed for the 4 hours on the 6th, when the methanol pump head was down, about 500 kilos of water would have been formed at the J-T valve.

Calculations made by other investigators showed that the methanol concentrations in the water was about 14 to 16% during this period and about half of this water therefore converted to hydrate at the J-T valve. This has been confirmed by experiment. Some of the hydrate that remained in the J-T drum would probably not have adhered firmly to the bottom due to its lack of stickiness at this methanol concentration.

The slurry of hydrate leaving the J-T drum would have settled out in horizontal pipework, flowed slowly along the bottom and eventually flowed through the booster pumps and into pools of water downstream. After 4 hrs the methanol pump head was shut down, these pools might well have been filled up with hydrates in the form of a thick slurry, able to withstand the drag from the flowing condensate.

In total, as much as 300 kilos of hydrate might have formed during this 4 hr period and it is questionable if any of it ever reached the condensate injection pump during this period. It would have loosely adhered in the J-T flashdrum, along horizontal piping and downstream of the booster pump(s).

As the methanol injection was restarted a new situation occurred in the J-T flashdrum. The hydrates would have been subjected to a higher methanol concentration as well as a larger water phase due to the increased methanol flow. Hydrates might then have been mobilised and started travelling down the pipework, picking up what was accumulated downstream.

Upon reaching the discharge of the booster pump the level and amount of water/hydrate would have risen until blocking occurred and the whole volume of hydrate slurry was swept out by the condensate in the form of a soft plug. By that time some hydrate slurry might already have "boiled" over from the vertical section and come to rest in the pipework upstream of the condensate injection pump. Upon arrival of the slurry plug, this would all have been swept out and into the pump (G-200B).

The hydrate slurry arriving at the condensate injection pump would have tended to block the exit valves, discharge chamber and possibly downstream pipework upon compression by the pistons. Such a plug may therefore have been responsible for the tripping of the condensate injection pump B at around 21.45 on the 6th. It may also have caused overpressurisation of pipework and subsequent leakage of hydrocarbons.

ACKNOWLEDGEMENTS

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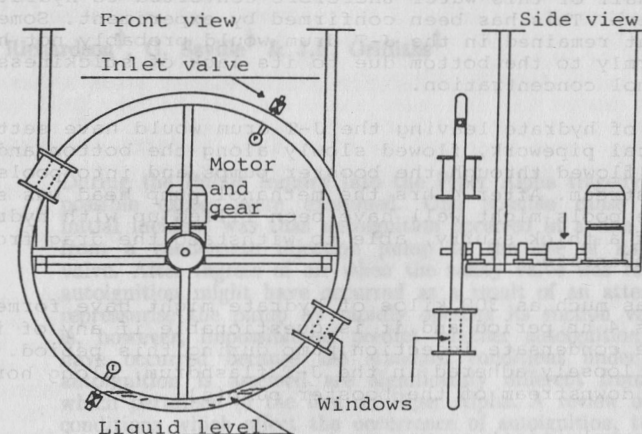


Fig. 1. PETRECO flow simulator. (Placed inside temperature controlled chamber).

Line A-B represent the trend when pumping mostly hydrocarbons through the pump after adding 15 WT % Methanol to the waterphase.
Line A-C represent the trend if mostly water phase was pumped through.
Note the increased hydrate potential.

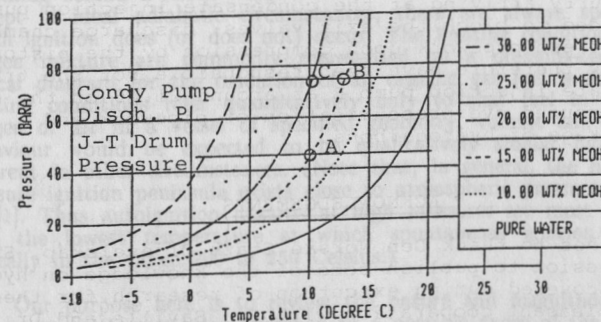


Fig. 2. Hydrate curve for Piper Alpha fluids entering J-T flashdrum.