

Mercury removal from Hydrocarbon Liquids

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Abstract

Mercury is found in an ever-increasing number of condensate fields worldwide. The level of mercury in the condensate can vary significantly depending on the location of the field.

Since mercury is known to cause corrosion of aluminium and liquid metal embrittlement (LME) of many of its alloys, as well as poisoning of metal based catalysts, it is important that it is removed to prevent equipment failures in plants where these metals are used. Removal of this contaminant not only protects plant equipment but also reduces the risk of personnel inhaling mercury vapour and dermal absorption of organic mercury during routine maintenance or shutdowns.

Johnson Matthey Catalysts have supplied PURASPEC absorbents to over 30 units in commercial operation for the removal of mercury from propane, butane and light / heavy naphtha streams. Removal of the mercury from those streams not only increases the value / marketability of the naphtha but also prevents poisoning of metal-based hydrogenation catalysts and equipment damage.

BP Netherlands Energie (BPNE) operate gas production platform P/15-D in the Dutch sector of the North Sea. Gas and Hydrocarbon condensate are brought onto the platform and go through a dehydration system before being exported via pipeline to on-shore storage

This paper will review the different steps taken by BPNE to select and install suitable mercury removal technology on the platform. Operational data will be presented in support of the technical evaluations.

Introduction

Mercury is a toxic and volatile metal that is a common contaminant in natural gas, natural gas liquids, and other hydrocarbon sources. Mercury can be present in hydrocarbon sources in the following three forms;

- Ionic
- Organic
- Elemental

Mercury level and species in condensate vary depending on the location of the field. Average values for the different regions are as summarised in Table 1.

Table 1 Reported Total Hg Concentration in Crude Oil

Type	Hg (ppb)	Notes
	mean	
Angola	2.7	Palanca
Angola	1.5	Soyo
UAE	5.7	
Colombia	12.3	
Congo	1.8	Kitina
Dubai	2.9	Nemba
Gabon	1.8	Rabi
Mexico	2.7	
Newfoundland	1.9	
Nigeria	1.0	Escravos
North Sea	9.3	Ekofisk
North Sea	2.5	Gullfaks
North Sea	4.7	Norne
Venezuela	5.0	Light
West Africa	3.5	Light

North Sea mercury levels have been increasing over the years. Due to the increase of the mercury level and to meet customer needs it became necessary for BP to install a mercury removal unit in 2004.

Condensate with high mercury levels is a product that cannot be sold easily. By installing a mercury removal unit BPNE is producing a more marketable product. This paper will review the different steps taken by BPNE to select and install suitable mercury removal technology on the platform. Operational data will be presented in support of the technical evaluations

Mercury Removal Systems

PURASPEC systems for hydrocarbon liquids are used to reduce the concentration of mercury and its compounds to very low levels in the product stream. Mercury needs to be removed from refinery products because they are used as feeds to numerous types of chemical manufacturing plants where mercury can lead to catalyst poisoning or catastrophic equipment failure. Thus many operators are finding it necessary to retrofit mercury guards on their liquid hydrocarbon streams to protect their downstream customers.

In order to design the optimum mercury removal system for a given application it is critical to understand the mercury speciation. Some hydrocarbon condensates can also contain significant amounts of suspended mercury compounds, most probably mercuric sulphide. Those colloidal forms

of mercury cannot be effectively removed using an absorbent bed and need to be removed upstream of the guard bed using a coalescer filter arrangement.

The location of the mercury removal unit (MRU) needs to be assessed based on the feedstock operating conditions and the type of mercury present. Commonly considered process locations for condensates include the main liquid feed, before the existing dehydrators and the common product lines (propane, butane, condensate lines) from the plant.

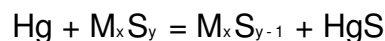
Mercury Removal from Hydrocarbon Condensate

Sulphur impregnated materials are not suitable for the removal of mercury from liquid hydrocarbons. This is due to the solubility of elemental sulphur in liquid hydrocarbons, particularly if aromatic species are present. Table 2 shows the equilibrium level of sulphur obtained with three liquid hydrocarbons.

Table 2: Solubility of Sulphur in Liquid Hydrocarbons at 25 °C

Hydrocarbon	Solubility (ppm)
Pentane	300
Heptane	500
Toluene	2500

Recognition of the disadvantages of the existing technologies to remove mercury from liquid hydrocarbons has led Johnson Matthey Catalysts to develop new fixed bed absorbents. These rely on the high reactivity of mercury with certain variable valency metal sulphides. Typically this reaction is:



The reactive metal is incorporated in an inorganic support. The absorbent is either supplied with the reactive sulphide present or it can be formed insitu by reaction with H₂S in the hydrocarbon to be treated. Two absorbents are available for hydrocarbon liquid treating; these are PURASPEC 5158 and PURASPEC 5157.

This approach has a number of advantages over conventional technology:

- The spent material can be recycled through metal smelters. This is made possible by the use of a combination of metals and an inorganic support that is compatible with smelting processes.
- The reactive species and the support have meso-porous structures with little affinity for hydrocarbons hence there are virtually no hydrocarbon losses.

- There is no risk of loss of sulphur by sublimation or dissolution. All sulphur species are securely bound as inorganic sulphides.
- Some organo-mercury compounds can be removed.

These features have resulted in the new products being retrofitted into a number of plants for LPG, naphtha and condensate purification. Typical examples of such units are shown in Table 3.

Table 3 Typical Examples of PURASPEC Mercury Removal Units on Liquid Hydrocarbons.

Location	Hydrocarbon	Rate (Tes/h)	Start Up	Mercury Content (ppbw)
UK	LPG	75	1997	60
M. East	Condensate	2 x 164	1999	10
Far East	LPG	182	2000	292
Far East	Naphtha	14	2002	20
Far East	Naphtha	0.22	2002	385
UK	Naphtha	130	2003	100
UK	Naphtha	120	2004	150
Netherlands	Condensate	80	2004	300
UK	Naphtha	156	2005	60

Case History – BPNE P1 5-D Mercury Removal Project

BP Netherlands operate platform P1 5-D in the Dutch sector of the North Sea. Gas and hydrocarbon condensate is brought onto the platform and goes through a dehydration system before being exported via pipeline to on-shore storage.

In 1998 when analysis first showed mercury in the condensate BPNE contacted Johnson Matthey Catalysts. A laboratory trial was undertaken at Johnson Matthey Catalysts research facilities in the North of England. The trial aim was twofold; first to establish the mercury species present in the condensate and second to prove that PURASPEC absorbent could remove the mercury present to the required specification of < 5 ppb w.

Laboratory work characterised the stream (see table 4).

Table 4 Properties of the condensate sample 1998

Colour, (Hazen No.)	125
Final Bpt	280 °C
> 200 °C Bpt	20%
Density	760 kg/m ³
Composition	C5 – C10
Total Mercury	250 ppb

Speciation showed mercury was present in all 3 forms; elemental, ionic and organic. The results are shown in table 3.

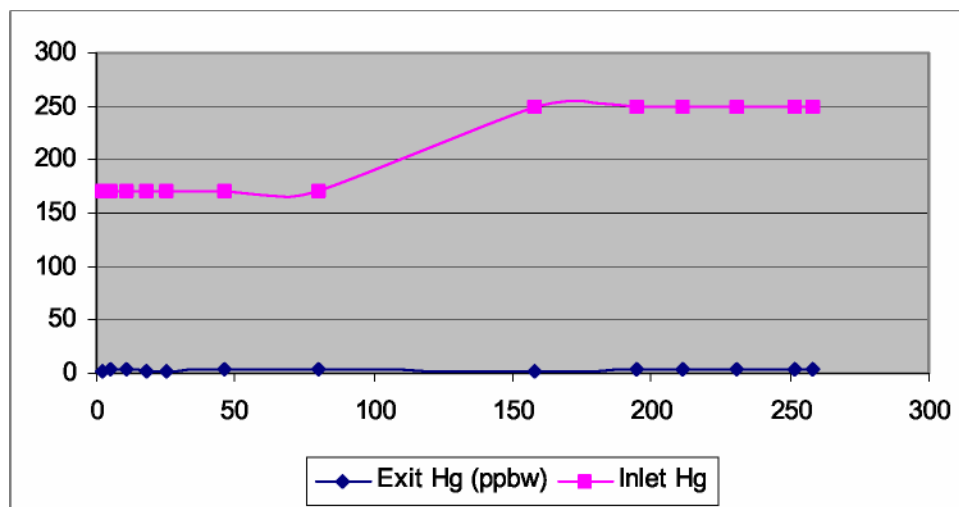
Table 5 Mercury Speciation Results 1998

Elemental Mercury	50%
DiMethyl Mercury	15%
DiEthyl Mercury	15%
Ionic Mercury	20%

This is an arduous duty. The majority of mercury removal units are located on refined streams.

A laboratory trial was designed to prove the performance of PURASPEC for mercury removal on this duty over a reasonable timeframe. Samples of the condensate were provided. These were fed to the test reactor over 250 hours. Regular analysis was carried out of the inlet and exit mercury levels. This showed that an exit level of < 5 ppbw was met consistently. The results are shown in fig 1.

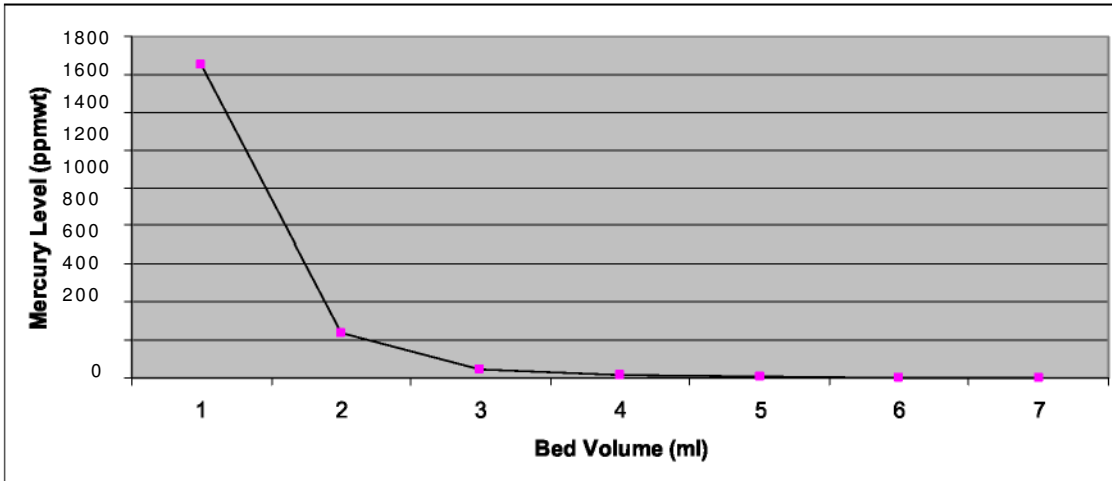
Fig 1 Laboratory Test Results



At the end of the test reactor run the bed was discharged. Care was taken to

ensure that the bed was removed 10% at a time. The discharged absorbent was then analysed to measure mercury pickup. The measured mercury pickup on the solids equalled the mercury pickup calculated from the inlet and exit mercury measurement. The mercury levels on the discharged absorbent are shown in fig. 2.

Fig 2 Discharged Solids Analysis



In 2003 mercury removal became a high priority. A sample of the current condensate was provided to Johnson Matthey Catalysts. This was analysed to characterize the stream and speciate the mercury to compare with the original sample. The results are shown in table 6.

Table 6 Properties of Condensate Sample 2003

Hazen No	20
> 200 °C Boiling	11.85%
Total Mercury	160 ppb
Elemental	100%
DiMethyl Mercury	Nil
DiEthyl Mercury	Nil
Ionic	Nil

The stream looked similar to the original sample. Limited laboratory work was carried out to check the performance of PURASPEC on the new stream. This showed positive results.

BP Netherlands Energie, working with Jacobs Engineering and Johnson Matthey Catalysts, designed and installed 2 mercury removal units for lead lag operation on P15-D. The process schematic is shown in figure 3.

The beds were loaded off-shore by Johnson Matthey Catalysts in August 2004 and commissioned in September 2004. Since then frequent analysis of the inlet and exit stream as well as 3 points down the absorbent bed have shown that the exit specification of < 5 ppb wt is being achieved. Measured data is shown in fig 4.

Figure 3 Process Schematic

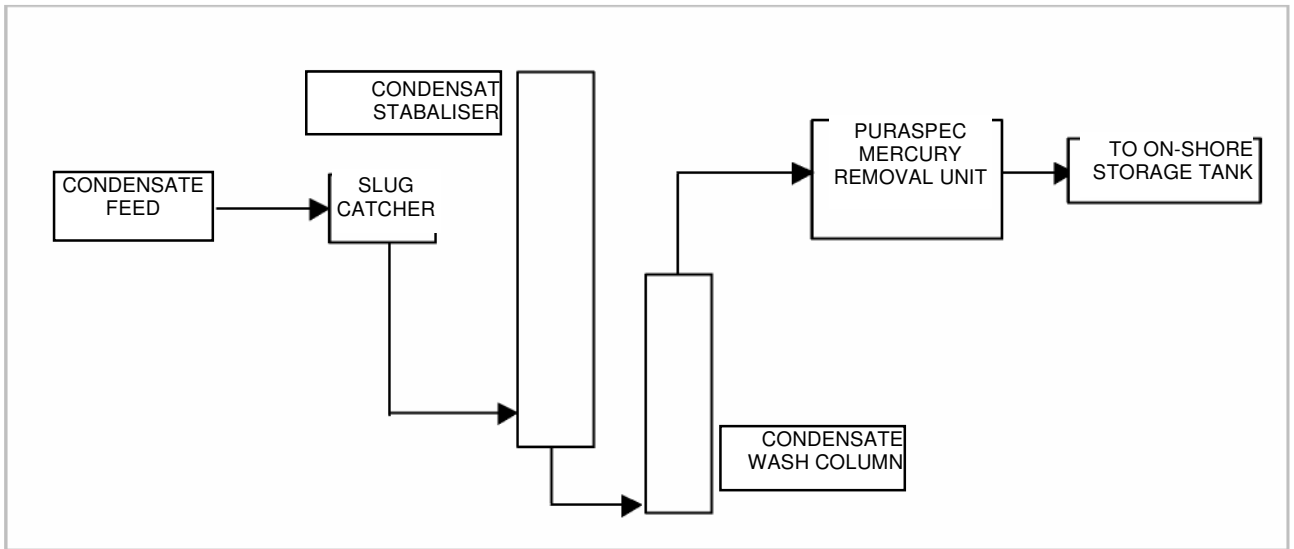
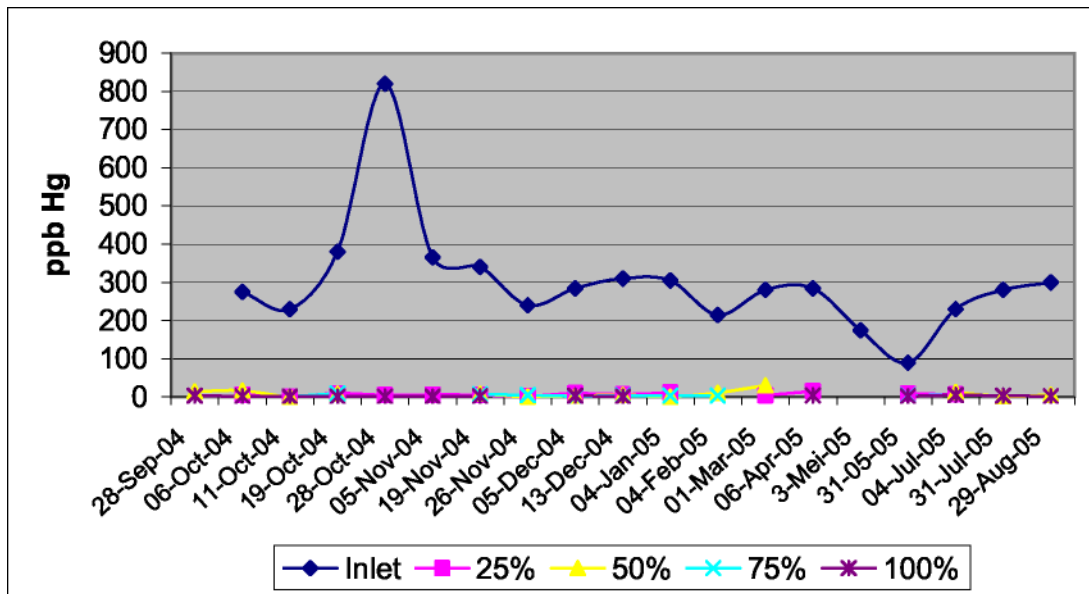
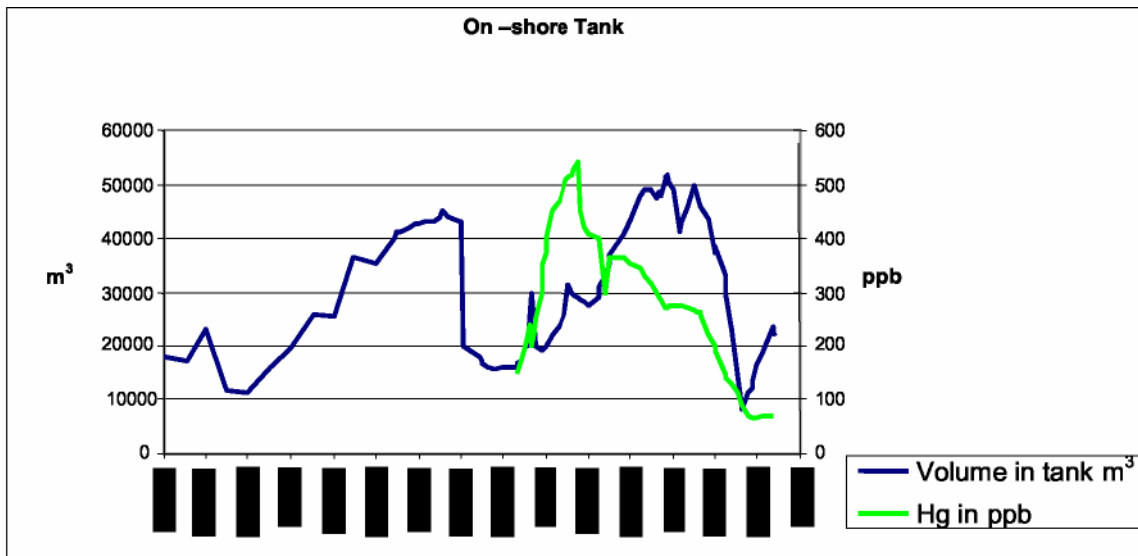


Fig 4 Hg levels through the bed



The condensate is stored in a 5000 m³ on-shore storage tank. The arrival of a stream of mercury free condensate has led to a considerable reduction in the mercury concentration of the contents of this tank.

Fig 5 Mercury Concentration in On-shore Storage Tank



Conclusion

This was a 'fast-track' project. It has moved from a PURASPEC bed being designed in December 2003 to installation and successful operation by September 2004.

The beds have been operating for 12 months, achieving the required outlet specification. This has opened up markets for BPNE condensate produced on the platform.

The project success was achieved by BPNE and Johnson Matthey Catalysts working closely together. Although the bed design was based on laboratory work on samples, the proven operation of other PURASPEC units gave BP confidence to use the PURASPEC technology for their application.