

Description

Mercury, even in very small amounts, is a toxic and corrosive metal. In media which are contacting metals such as aluminium during their processing and storage, mercury causes an important corrosion and therefore has to be removed. Also media discharged to the environment have to be substantially free from mercury because of its toxicity.

G.J. de Jong and C.J.N. Rekers describe in Proceedings of the First World Mercury Congress, published in the Journal of Chromatography, Volume 102 (1974), pages 443 - 451 a process for the removal of mercury from waste water by using an ion exchange resin containing active thiol groups. It is emphasized that this resin reacts only with ionic mercury, i. e. that all metallic mercury in the waste water must be oxidized before it is contacted with the ion exchange resin.

Mercury very often also occurs in organic media, especially non-polar organic media like hydrocarbon mixtures. A typical example is natural gas which can contain up to 180 $\mu\text{g}/\text{Nm}^3$ (see e.g. NAM recovers mercury produced with Dutch natural gas in The Oil and Gas Journal of April 1972, pages 72 - 73).

The purification of natural gas includes a partial condensation at which the raw gas is cooled to separate higher boiling components like C_4 - and higher hydrocarbons or aromatics like benzene and its derivatives, toluene and its derivatives, etc. At this step also the major quantity of the mercury contained in the natural gas is separated and accumulates in the obtained natural gas condensate. Before further processing the gas condensate such as by steam cracking the mercury being present in predominantly elemental form in quantities up to 105 $\mu\text{g}/\text{kg}$ has to be removed in an efficient manner.

It is known to remove elemental mercury from natural gas by contacting the same with sulfur-impregnated activated carbon, metals, like finely divided copper, and metal sulfides, like iron sulfide, or by oxidation of the mercury by strongly oxidizing solutions (Hydrocarbon Processing, November 1980, pages 237 - 240).

By these methods it is, however, not possible to remove mercury from organic media because of the dissolution of sulfur in the organic media and sulfur being unwanted in the further process. Additionally, metals and metal sulfides have the disadvantage of a relatively short life time.

Therefore, the object of the invention is the provision of an effective process for removing mercury up to the lower ppb-range from organic, especially non-polar, media like natural gas, liquefied natural gas, and most preferably natural gas condensates.

According to the present invention mercury is removed from organic, especially non-polar, media, like hydrocarbon media, by contacting the media with a solid adsorbents containing active SH-groups.

Accordingly, the present invention is based on the surprising discovery that solid adsorbents containing active SH-groups are capable of absorbing mercury being present in organic media in finely divided or even atomic form. It is surprising that this absorption occurs since the prior art - as outlined above - is teaching that solid adsorbents having active thiol groups are only capable of absorbing ionic (oxidized) mercury being present in aqueous media like waste water.

Preferably the solid adsorbens is an ion exchange resin.

As already mentioned the process of the present application is applicable to the removal of mercury from any kind of organic media, especially non-polar media like hydrocarbon media, in liquid and also vaporous form. Preferably, however, the process of the present application is applied to the removal of mercury from natural gas condensates, i. e. liquid hydrocarbon mixtures, the components of which have higher boiling points than the main constituents of natural gas. Therefore, in the following the process of the present invention is explained by reference to natural gas condensates but it should be emphasized that it is also applicable to other organic media.

The ion exchange resins containing active thiol groups used according to the present invention preferably are macroporous copolymers of styrene and divinylbenzene, for example the ion exchange resin IMAC TMR of Rohm & Haas Company, Philadelphia, USA, which apart from thiol groups also contains sulphonic acid groups. This ion exchange resin is supplied in form of beads having a particle size of 0,3 to 1,2 mm and a thiol capacity of 1400 meq/l, and being regenerable by concentrated hydrochloric acid.

To remove effectively mercury from natural gas condensates these condensates should be contacted with the ion exchange resin with a residence time of more than 30 seconds.

According to the composition of the medium to be treated the temperature at which the medium is contacted with the ion exchange resin can vary between -30°C and 60°C and preferably between 0 and 60°C , ambient temperature being the most preferred treating temperature.

Normally, the process of the present invention is carried out under atmospheric pressure, however, in certain cases (if for example the vapour pressure of the medium to be treated is high) it can also be advisable to apply superatmospheric pressure.

The residual mercury in the treated media preferably is measured by the following method:

A 50 - 100 g sample is added to a conical flask containing 10 ml of an 1:1 (v/v) mixture of H_2SO_4 and 3 g KMnO_4 in 60 ml water. Then the conical flask at the top is equipped with a reflux condenser, and the flask content is stirred for 30 minutes. Subsequently the mixture is brought to boiling and boils gently during one hour. After cooling the solution to room temperature 1 g hydroxylammoniumchloride is added, the flask is carefully shaken until the black precipitate disappears, the solution is transferred into a separation funnel and washed therein several times with water which is also added to the separation funnel. After the phases have separated the underlayer (waterphase) is added to a graduated 100 ml-flask, and the separation funnel is washed several times with little water, and this water is also added to the graduated flask. The flask is filled up to the mark with water and the mixture is thoroughly mixed.

The obtained solution is now ready for measuring the mercury content by the cold vapour AAS method (ISO-draft ISO/CT-158 SC/2; see also "Analysis of petroleum of trace metals" by Hofstadter, Milner & Runnels, American Chemical Society, pages 133 to 148).

Residual mercury measurements according to the above mentioned method have shown that according to the process of the present invention more than 97 % of the mercury being present in the starting medium can be removed.

The following example illustrates the process of the present invention without limiting its scope.

Example

A natural gas condensate containing mercury in an amount of 35 $\mu\text{g/kg}$ at a temperature of 25°C and at a pressure of 1 bar (absolute) is passed in upflow direction through a glass column having a volume of 64 cm^3 , a height of 32 cm and an internal diameter of 1,6 cm, and being filled with ion exchange resin particles (particle diameters between 0,3 and 1,2 mm) of IMAC TMR of Rohm and Haas Company, Philadelphia, USA in an amount of 50 g. The gas condensate is passed through the column at a rate of 500 g/hour (residence time: 2 minutes).

As determined by the cold vapour AAS method the mercury content of the effluent is less than 1 $\mu\text{g/kg}$.

Using the same column the flow of gas condensate can be increased up to 2000 g/hour without lowering the above quoted degree of mercury recovery.

Claims

1. A process for removing mercury from a non-polar organic medium, characterized in that the medium is contacted with a solid adsorbent containing active SH-groups.
2. A process according to claim 1, characterized in that the solid adsorbent is an ion-exchange resin.
3. A process according to claim 2, characterized in that the ion-exchange resin is a macroporous copolymer of styrene and divinylbenzene containing said active thiol-groups.
4. A process according to anyone of the claims 1 to 3, characterized in that the medium to be treated is predominantly a mixture of hydrocarbons.
5. A process according to anyone of the claims 1 to 4, characterized in that the medium to be treated is a gas condensate, substantially free from lower boiling gas components, obtained by the partial condensation of natural gas.
6. A process according to anyone of the claims 1 to 5, characterized in that the mercury-containing medium is contacted with the solid adsorbent during a residence time of more than 30 seconds.
7. A process according to anyone of the claims 1 to 6, characterized in that the mercury-containing medium is contacted with the solid adsorbent at a temperature between -30°C and 60°C, preferably between 0 and 60°C.
8. Use of a process according to anyone of the claims 1-7 for the removal of mercury from a gascondensate prior to the cracking of said gas condensate.

Revendications

1. Procédé d'élimination du mercure d'un milieu organique non polaire, caractérisé en ce qu'on met en contact le milieu avec un adsorbant solide contenant des groupes actifs SH.
2. Procédé selon la revendication 1, caractérisé en ce que l'adsorbant solide est une résine échangeuse d'ions.
3. Procédé selon la revendication 2, caractérisé en ce que la résine échangeuse d'ions est un copolymère macroporeux styrène/divinylbenzène contenant lesdits grou-



The residual mercury in the treated media preferably is measured by the following method:

A 50 - 100 g sample is added to a conical flask containing 10 ml of an 1:1 (v/v) mixture of H_2SO_4 and 3 g $KMnO_4$ in 60 ml water. Then the conical flask at the top is equipped with a reflux condenser, and the flask content is stirred for 30 minutes. Subsequently the mixture is brought to boiling and boils gently during one hour. After cooling the solution to room temperature 1 g hydroxylammoniumchloride is added, the flask is carefully shaken until the black precipitate disappears, the solution is transferred into a separation funnel and washed therein several times with water which is also added to the separation funnel. After the phases have separated the underlayer (waterphase) is added to a graduated 100 ml-flask, and the separation funnel is washed several times with little water, and this water is also added to the graduated flask. The flask is filled up to the mark with water and the mixture is thoroughly mixed.

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5. A process according to anyone of the claims 1 to 4, characterized in that the medium to be treated is a gas condensate, substantially free from lower boiling gas components, obtained by the partial condensation of natural gas.
6. A process according to anyone of the claims 1 to 5, characterized in that the mercury-containing medium is contacted with the solid adsorbent during a residence time of more than 30 seconds.
7. A process according to anyone of the claims 1 to 6, characterized in that the mercury-containing medium is contacted with the solid adsorbent at a temperature between -30°C and 60°C, preferably between 0 and 60°C.
8. Use of a process according to anyone of the claims 1-7 for the removal of mercury from a gas condensate prior to the cracking of said gas condensate.

Revendications

1. Procédé d'élimination du mercure d'un milieu organique non polaire, caractérisé en ce qu'on met en contact le milieu avec un adsorbant solide contenant des groupes actifs SH.
2. Procédé selon la revendication 1, caractérisé en ce que l'adsorbant solide est une résine échangeuse d'ions.
3. Procédé selon la revendication 2, caractérisé en ce que la résine échangeuse d'ions est un copolymère macroporeux styrène/divinylbenzène contenant lesdits grou-



pes thiol actifs.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que le milieu à traiter est principalement un mélange d'hydrocarbures. 5
5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le milieu à traiter est un condensat gazeux sensiblement exempt de composants gazeux à bas point d'ébullition, qu'on obtient par condensation partielle du gaz naturel. 10
6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce qu'on met en contact le milieu contenant du mercure avec l'adsorbant solide pendant une durée de séjour de plus de 30 secondes. 15
7. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce qu'on met en contact le milieu contenant du mercure avec l'adsorbant solide à une température comprise entre -30 et 60 °C, de préférence entre 0 et 60 °C. 20 25
8. Utilisation d'un procédé selon l'une quelconque des revendications 1 à 7, pour l'élimination du mercure à partir d'un condensat gazeux avant le craquage dudit condensat gazeux. 30

Patentansprüche

1. Verfahren zum Entfernen von Quecksilber aus einem nichtpolaren organischen Medium, dadurch gekennzeichnet, daß das Medium mit einem festen Adsorbens, das aktive SH-Gruppen enthält, in Berührung gebracht wird. 35 40
2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das feste Adsorbens ein Ionenaustauscherharz ist. 45
3. Verfahren gemäß Anspruch 2, dadurch gekennzeichnet, daß das Ionenaustauscherharz ein die aktiven Thiolgruppen enthaltendes makroporöses Copolymer von Styrol und Divinylbenzol ist. 50
4. Verfahren gemäß einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das zu behandelnde Medium überwiegend ein Gemisch von Kohlenwasserstoffen ist. 55
5. Verfahren gemäß einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das zu behan-

delnde Medium ein Gaskondensat ist, das im wesentlichen frei von niedrig siedenden Gas-komponenten ist und durch teilweise Kondensation von Erdgas erhalten wird.

6. Verfahren gemäß einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das Quecksilber enthaltende Medium mit dem festen Adsorbens während einer Verweilzeit von mehr als 30 Sekunden in Berührung gebracht wird.
7. Verfahren gemäß einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Quecksilber enthaltende Medium mit dem festen Adsorbens bei einer Temperatur zwischen -30 °C und 60 °C, vorzugsweise zwischen 0 und 60 °C, in Berührung gebracht wird.
8. Anwendung eines Verfahrens gemäß einem der Ansprüche 1 bis 7 zur Entfernung von Quecksilber aus einem Gaskondensat vor dem Cracken des Gaskondensats.