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(54) **Mercury removal.**

(57) A process for the removal of mercury from a stream wherein an absorbent comprising a metal sulphide is prepared in situ, preferably by the stream also containing a sulphur compound thereby concomitantly preparing the mercury absorbent and absorbing the mercury, such that the formation of ineffective and undesired metal compounds e.g. sulphates is avoided.

EP 0 480 603 A2

This invention relates to a process for the removal of mercury from a gaseous or liquid stream.

GB-B-1533059 discloses the use of a pre-sulphided absorbent comprising copper sulphide for the absorption of mercury from a natural gas stream containing mercury. The pre-sulphided absorbent is prepared by forming a precursor comprising a copper compound, e.g. an extrudate comprising basic copper carbonate and a refractory cement binder, and then contacting the precursor with a gaseous stream containing a sulphur compound, e.g. hydrogen sulphide, so as to fully sulphide the copper compound. The pre-sulphided absorbent is then used to remove mercury from a sulphur-free natural gas stream. It is also shown that an absorbent comprising copper in the reduced, i.e. metallic, state is less effective at absorbing mercury than the pre-sulphided absorbent.

Japanese kokoku JP-75001477 shows that a pre-sulphided absorbent comprising copper sulphide is capable of absorbing mercury from a stream of electrolytic hydrogen containing mercury.

It has now been found that a pre-sulphided absorbent comprising a metal sulphide, in particular a pre-sulphided absorbent comprising copper sulphide, may exhibit a change in its mercury absorption capacity during storage such that a freshly pre-sulphided absorbent is more readily able to absorb mercury than a similar absorbent which has been stored for subsequent use. It has also been found that the ability of an absorbent comprising a metal sulphide to absorb mercury is dependent on the conditions under which the sulphiding is conducted. Furthermore, it has also found that it is possible to improve the performance of a mercury removal process using an absorbent comprising a metal sulphide by concomitantly forming the metal sulphide during the absorption of the mercury.

Accordingly the present invention provides a mercury removal process comprising contacting a mercury-containing feed stream with an absorbent comprising a metal sulphide capable of absorbing mercury and wherein the absorbent is formed by contacting in situ a precursor comprising a metal compound capable of forming the metal sulphide with a first stream containing a sulphur compound.

The present invention may be used to treat both liquid and gaseous feed streams. Gaseous feed streams which are susceptible to being treated by the present invention include those which inherently contain both mercury and a sulphur compound e.g. certain natural gas streams, or a mercury containing gaseous stream to which a sulphur compound has been added to effect mercury absorption. Suitable liquid streams include mercury containing LPG and naphtha streams.

As stated above, conventional absorbents comprising copper sulphide are pre-sulphided, i.e. they are sulphided prior to use, and are then often stored in contact with air. It has now been found that during storage substantial quantities of copper sulphate are formed which is significantly less effective as an absorbent than copper sulphide. Thus, the presence of a metal sulphate is undesirable and it is therefore preferred that the absorbent used in the present invention is substantially sulphate free. To avoid the formation of the metal sulphate, the absorbent used in the present invention is sulphided in situ, i.e. it is not pre-sulphided and stored subsequent to use in contact with air or an other oxygen containing gas. Thus, the precursor may be sulphided using a first stream which contains a suitable sulphur compound to form the absorbent and then held in-situ in a non-sulphate forming environment. It is preferred, however, that the sulphiding of the precursor and the absorption of mercury occur together, i.e. they are concomitant, thereby avoiding the need for a separate sulphiding process and the subsequent storage difficulties. Thus, the present invention may be advantageously used on streams which contain both mercury and sulphur compounds.

Preferably the concomitant absorption of mercury and sulphur is conducted at a temperature below 100°C in that at such temperatures the overall capacity for mercury absorption is increased. Temperatures as low as 20°C may be used to good effect in the present invention.

The mercury may be in the form of mercury vapour, organomercuric, or organomercurous compounds. Typically the concentration of mercury in a gaseous feed stream is from 0.01 to 500 ug.Nm⁻³, and more usually between 10 to 200ug.Nm⁻³.

The sulphur compound used to sulphide the precursor may be one or more sulphur compounds such as hydrogen sulphide, carbonyl sulphide, mercaptans and polysulphides. Where concomitant sulphiding and mercury absorption occurs the amount of sulphur compound that is present depends on the type of sulphur compound and metal compound used. Usually, a concentration ratio, as defined by the ratio of sulphur compound (expressed as hydrogen sulphide) concentration (v/v) to mercury concentration (v/v), of at least one, and preferably of at least 10 is used so that the precursor is sufficiently sulphided. Should the initial concentration of the sulphur compound in the feed stream be below the level necessary to establish the desired ratio of sulphur compound to mercury compound concentration then it is preferred that the concentration of the sulphur compound is increased by any suitable method, e.g. by the addition of further quantities of the sulphur compound, or by the use of a molecular sieve or semi-permeable membrane to selectively increase the concentration of the sulphur compound.

The metal may be any which provides a metal compound which shows a suitable capacity for being sulphided and for mercury absorption. Examples of suitable metals are iron and copper, and in particular copper. Certain other metals, however, are generally unable to provide either compounds which can be suitably sulphided, e.g. aluminium, or sulphided compounds which can adequately absorb mercury e.g. zinc. Nevertheless, a compound of such an other metal may be present as a binding or support agent which improves the structural integrity of the absorbent, and/or as a promoter which enhances the sulphiding of the precursor and/or the absorption of mercury by the absorbent.

A metal compound suitable for use in an absorbent precursor is one which may be readily sulphided and may include the oxide, carbonate, and/or basic carbonate. A particularly suitable metal compound is thus basic copper carbonate.

The precursor comprising the metal compound may be in any suitable form, e.g. as a granule, extrudate, or tablet. Particularly effective absorbents are those which are prepared from precursors having a capacity to be highly sulphided. Thus, it is preferred that the amount of sulphide forming compound of the metal present in the precursor is such that the precursor may be sulphided to achieve a sulphur loading of at least 15% w/w, and particularly at least 20% w/w.

The present invention is illustrated by the following examples.

Example 1

A freshly sulphided material containing copper and zinc sulphides, having a total sulphur content of 19% w/w was tested for its ability to remove mercury from a simulated natural gas feed stream. The material had previously been sulphided at 20°C and 1 atm. using a natural gas stream which was saturated with water, and contained 1% v/v hydrogen sulphide.

Mercury removal was assessed at 20°C, 1 atm., by contacting the sulphided material at a space velocity of 10000 hr⁻¹ with methane containing 1.8 ppm mercury. Example 2

Example 1 was repeated except that the sulphided material was stored under ambient conditions, and in contact with air, for 8 months prior to the mercury removal assessment.

The results of Examples 1 and 2 are shown in Table 1.

Table 1

Days on line	Mercury Slip %	
	Example 1	Example 2
<1	0.0	100.0
9	0.0	-
14	2.5	-
16	5.0	-
18	7.5	-
19	10.0	-

It can thus be seen that the ability of the sulphided material to remove mercury diminishes on storage. Analysis of the materials used in Examples 1 and 2 showed the presence of copper sulphate in the material of Example 2 and the absence of copper sulphate in the material of Example 1.

Example 3

Example 1 was repeated using a sulphided material containing 6.2% w/w of sulphur.

Example 4

Example 3 was repeated except that the sulphiding was conducted at a temperature of 110°C, to a sulphur loading of 17.7% w/w.

Example 5

Example 4 was repeated except that the sulphur loading was to 24% w/w.

The results of Examples 3 to 5 are shown in Table 2.

Table 2

Hours on-line	Mercury Slip %		
	Example 3	Example 4	Example 5
24	0.0	1.0	0.0
48	0.0	2.4	0.0
72	0.0	3.8	0.0
96	4.5	5.8	0.0
120	9.4	>12.5	0.0
144	12.1	-	0.6

It can thus be seen that although the material of Example 4 was laden with more than twice the amount of sulphur than that of Example 3, the material of Example 3 was superior in performance to that of Example 4. Example 5 shows that for materials which have been sulphided under the same conditions, the greater the sulphur loading the more mercury can be absorbed before mercury slip occurs.

Example 6

Example 1 was repeated using a material of the same composition as that of Mass A of UK patent, GB-B-1533059.

The freshly sulphided material was similarly assessed for its mercury removal capacity. After 2 days on-line a mercury slip of 2.5% was observed. The mercury slip increased approximately at a rate of 2.5% per day until the end of the assessment on the fifth day.

Example 7

In this Example the non-sulphided starting material of Example 1 was placed in sample baskets, and inserted into an industrial operating unit used for the removal of sulphur compounds, principally hydrogen sulphide (60 - 70 ppm), from natural gas containing 11% v/v carbon dioxide. The natural gas also contained mercury as a trace component. The unit was operated at about 70°C, and 50 bar. After a period of time on line, the sample baskets were retrieved and analysis of the material for sulphur and mercury contents performed.

The material was shown to be sulphided and to have a sulphur content of 18.1%. Furthermore, the material was shown to have a mercury content of 2.2% w/w.

Example 8

At the same time as the sample baskets of Example 7 were inserted into the operating unit, additional sample baskets containing a zinc oxide sulphur absorbent were also inserted. These were then analysed in the same manner as those of Example 7.

The zinc oxide sulphur absorbent was shown to have a sulphur content of 17.3% w/w. No mercury was shown, however, to have been absorbed by the material.

Claims

1. A mercury removal process comprising contacting a mercury-containing feed stream with an absorbent comprising a metal sulphide capable of absorbing mercury and wherein the absorbent is formed by contacting in situ a precursor comprising a metal compound capable of forming the metal sulphide with a first stream containing a sulphur compound.

2. A process as claimed in claim 1 wherein the feed stream contains a sulphur compound and comprises at least part of the first stream and the first stream contacts the precursor such that the formation of the metal sulphide is concomitant with the absorption of mercury from the feed stream.

3. A process as claimed in claim 2 wherein the first stream contacts the precursor at a temperature not exceeding 100°C.
4. A process as claimed in either claim 2 or claim 3 wherein the concentration ratio, as defined by the ratio of concentration of the sulphur compound (v/v) to the concentration of the mercury compound (v/v), in the first stream on contact of the precursor with the first stream is at least 1:1.
5. A process as claimed 4 wherein the initial concentration of the sulphur compound in the first stream prior to contact of the precursor with the first stream is such that the concentration ratio is below 1:1, and the concentration of the sulphur compound is increased such that the concentration ratio on contact of the precursor with the first stream is at least 1:1.
6. A process as claimed in any one of claims 1 to 5 wherein the sulphur compound is at least one of hydrogen sulphide, carbonyl sulphide, mercaptans and polysulphides.
7. A process as claimed in any one of claims 1 to 6 wherein the metal is at least one of copper and iron.
8. A process as claimed in any one of claims 1 to 7 wherein the metal compound is basic copper carbonate.
9. A process as claimed in any one of claims 1 to 8 wherein the precursor can be sulphided so as to contain a sulphur content of at least 15% w/w.
10. A process as claimed in any one of claims 1 to 9 wherein the feed stream is gaseous and has a mercury content from 0.01 to 500 $\mu\text{g.Nm}^{-3}$.