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(54) Title: PROCESS FOR THE DISPOSAL OF SULFUR

(57) Abstract: Process for the disposal of sulfur which comprises melting the sulfur, optionally in the presence of hydrogen sulfide, and injecting the molten sulfur into geological structures having a temperature ranging from 90 to 160 °C.



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PROCESS FOR THE DISPOSAL OF SULFUR

The present invention relates to a new process for the disposal of sulfur.

10 More specifically, the present invention relates to a new process for the disposal of sulfur coming from the purification treatment of hydrocarbons of a fossil nature, for example crude oil or natural gas.

15 It is well known that sulfur can be present in considerable quantities in both extracted crude oil and natural gas. In this gas, the sulfur can be present in the form of H_2S in a percentage molar quantity which can reach 10% and in particular certain cases it can even exceed 20%, referring to gas.

20 When present in high concentrations in gas, the hydrogen sulfide is separated using various systems, of which the most widely used is absorption in solutions of ethanol amines. Once it is in the concentrated state, the hydrogen sulfide is transformed into elemental sulfur by means of
25 the Claus process. At this point, it is necessary to allo-

cate the sulfur which, for the last few years and potentially for tens of years to come, has a market characterized by an excessive offer with respect to the demand. Sulfur is normally stored in elemental form as huge blocks
5 which require continual monitoring and treatment of the runoff water to avoid the acidification of the ground and surrounding underground water. In addition to this, there is an increasingly strict legislation on the part of states containing oil fields or natural gas reservoirs, which in
10 some cases impose heavy penalties for the storage of recovered sulfur.

The Applicants have now found an innovative process for the elimination of said large quantities of sulfur which envisages its injection into the ground by pumping it
15 in the liquid state into adequate geological structures. These structures can consist of the field itself from which the crude oil or associated gas has been extracted or other adequate geological structures, such as abandoned mines or saline aquifers.

20 Thanks to the solution, object of the present invention, a permanent sulfur storage is obtained without any risk of its leaving the surface and contaminating usable groundwater or negatively interfering with the extraction process of crude oil/gas. Large accumulations of sulfur do
25 in fact exist in nature in indefinitely stable geological

structures and without having a negative impact on the surrounding environment.

An object of the present invention therefore relates to a process for the disposal of sulfur which comprises
5 heating and melting the sulfur, optionally in the presence of hydrogen sulfide, and injecting the molten sulfur, in liquid and homogeneous form, into geological structures having a temperature ranging from 90 to 160°C.

The present invention envisages the pumping of sulfur
10 in liquid form through surface pipes, well pipes and receiving geological structures. The molten elemental sulfur can come directly from the Claus process or from a surface storage site.

The pressure necessary for pumping the liquid obtained
15 from the liquefaction of sulfur into a pipe can be calculated with the general formula:

$$\Delta P = 2f \cdot \rho \cdot u_m^2 L / D_{eq}$$

wherein L is the length of piping used for injection into the geological structure. D_{eq} its equivalent diameter, u_m
20 the average rate of the fluid pumped, ρ the density of the fluid pumped and f the friction factor which is a function of the roughness of the pipe and Reynolds number:

$$Re = D_{eq} \cdot u_m \cdot \rho / \mu$$

wherein μ is the kinematic viscosity of the fluid. The
25 pumping device can be represented by a conventional pump

capable of processing fluids at temperatures ranging from 90°C to 160°C. The viscosity values of the sulfur in the molten state within the temperature limits indicated are specified in Table 1 below.

5

Table 1

Viscosity of molten sulfur in relation to the temperature

10

Temperature (°C)	μ (cPoise)
119	11.45
125	10.31
132	8.84
140	7.67
150	6.62
157	6.72
160	11.6

15

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The geological structures which are appropriate for receiving the molten sulfur are those having temperatures ranging from 90°C to 160°C and, preferably, those forming the reservoir itself from which the crude oil or natural gas containing sulfur in the form of organic compound or hydrogen sulfide, are extracted. Alternatively, geological structures can be used, in a remote position with respect to the reservoir and having structural characteristics suitable for receiving and preserving the molten sulfur.

25

For the application of the present invention, either

matrix geological structures or fractured structures, naturally or induced, can generally be used. In all cases, the pressure and maximum injection flow-rate of the fluid forming the molten sulfur, optionally mixed with hydrogen sulfide, can be determined by calculations and measurements well known to experts in stimulation treatment of production wells or the production and running of water re-injection wells.

The present invention requires the injection of sulfur in liquid form with a low viscosity. In the case of pure elemental sulfur, the appropriate conditions for the application of the present invention are obtained for temperatures ranging from 119°C to 160°C. The field of application of the disposal process of sulfur, object of the present invention, can be enlarged by mixing elemental sulfur with other compounds capable of lowering the melting point of the mixture. A valid and economical system for reducing the melting point of sulfur consists in mixing it with H₂S under pressure. Table 2 below indicates the melting points (T_m) of sulfur in the presence of H₂S at different pressure values. In this way it is possible to lower the melting point of sulfur from 119°C to 90°C approximately.

Table 2Influence of the H₂S pressure on the T_m of sulfur

Melting point of sulfur (°C)	H ₂ S pressure (bar)
119	0
115	1
111	12
106	24
100	39
100	40
94	58
91	80
91	90
90	110
90	125
90	155

This lowering of the melting point of sulfur is verified, even if to a lesser degree, also when hydrogen sulfide is mixed with other gases without an analogous effect, such as, for example, methane or carbon dioxide. From the following table it can be observed how, at a fixed pressure (for example 200 bar) the melting point of sulfur decreases with an increase in the concentration of H₂S in the mixture with methane.

Table 3

Influence of the concentration of H₂S in methane on the
melting point of sulfur at 200 bar

5	Melting point of sulfur (°C)	H ₂ S percentage in methane
	119	0
	117	4.5
	115	9
	114	14
10	109	25
	92	100

The possibility of applying the present invention also using hydrogen sulfide mixed with methane can prove to be economically advantageous if the receiving geological structure is at a sufficiently high temperature and the use of the mixture with methane can avoid the necessity of a separation process of methane from hydrogen sulfide.

Finally, it should be noted that the disposal system of sulfur, object of the present invention, allows part of the hydrogen sulfide separated from the associated gas to be used to fluidize the sulfur produced with the Claus process, thus reducing the total volume of H₂S to be sent to the Claus process itself.

Therefore, with respect to the practical embodiment of the present invention, the disposal process of sulfur

should therefore be effected by selecting a suitable receptive geological structure having a temperature ranging from 90°C to 160°C, optionally mixing the sulfur with hydrogen sulfide (preferably pure) so that the melting point of the
5 mixture is lower than or equal to that of the receiving geological structure, heating the sulfur (or mixture) to a temperature which is sufficiently higher than the melting point so that, during the pumping process at the surface and in the well, the sulfur (or mixture) remains in the
10 liquid state and, finally, pumping the sulfur (or mixture) into the reservoir through possibly insulated pipes.

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CLAIMS

- 1) A process for the disposal of sulfur which comprises melting the sulfur, optionally in the presence of hydrogen sulfide, and injecting the molten sulfur into geological structures having a temperature ranging from 90 to 160°C.
- 2) The process according to claim 1, wherein the disposed sulfur comes from purification treatment of hydrocarbons of a fossil nature (crude oil) or from natural gas.
- 3) The process according to claim 1 or 2, wherein the molten elemental sulfur come directly from the Claus process.
- 4) The process according to claim 1 or 2, wherein the elemental sulfur comes from a surface storage site.
- 5) The process according to any of the previous claims, wherein the hydrogen sulfide is used in a mixture with other gases which do not have the capacity of reducing the melting point of element sulfur.
- 6) The process according to claim 5, wherein the gas mixed with hydrogen sulfide is methane or carbon dioxide.
- 7) The process according to any of the previous claims, wherein the hydrogen sulfide is that sepa-

rated from the natural gas with which it is associated.

- 8) The process according to any of the previous claims, wherein the geological structures which are appropriate for receiving molten sulfur are those forming the reservoir from which the crude oil or natural gas containing sulfur are removed.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B09B B65G E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 582 025 B2 (R. PICKREN) 24 June 2003 (2003-06-24) column 1, line 14 - line 29 column 2, line 59 - column 4, line 40 column 5, line 63 - column 6, line 30 column 11, line 30 - line 47 column 12, line 35 - line 65	1-7
A	figures 1,3	8
A	US 4 428 700 A (W. LENNEMANN) 31 January 1984 (1984-01-31) claim 1	1
A	US 3 690 377 A (B. KNIGHT) 12 September 1972 (1972-09-12) abstract	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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