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E. S. D.

REF: INTEVEP, S.A.

Expediente No.02 014.503 - Solicitud de Patente

**Titulada: MÉTODO PARA RETIRAR H₂S Y CO₂ DE CORRIENTES
DE CRUDO Y GAS**

RAMIRO CASTRO DUQUE, vecino de Bogotá, portador de la tarjeta profesional No. 1003, obrando como apoderado de la sociedad, INTEVEP, S.A., según lo acredita el documento de poder protocolizado en esa División bajo el No. 14558, para dar cumplimiento al requerimiento notificado por fijación en lista el 21 de Marzo de 2002, y de acuerdo con los artículos 38 y 39 de la Decisión 486 de la comisión de la Comunidad Andina, me permito anexar al presente escrito los siguientes documentos:

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Cra 7 No. 16-56 Piso 9

Bogotá, Abril 19, 2002

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A. Patent Application No.(s)

03/01/2001 BHUYENI 00000005 09791178
02 FC1581 40.00 IP

B. Patent No.(s)

09791178

Additional numbers attached? ☐ Yes ☒ No

5. Name and address of party to whom correspondence concerning document should be mailed:

Name: Gregory P. LaPointe
Internal Address: Bachman & LaPointe, P.C. Suite 1201

Street Address: 900 Chapel Street
City: New Haven State: CT ZIP: 06510

6. Total number of applications and patents involved: 1

7. Total fee (37 CFR 3.41) \$ 40.00
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PATENT
REEL: 011662 FRAME: 0768

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 and is entitled **METHOD FOR REMOVING H₂S AND CO₂ FROM CRUDE AND GAS STREAMS**

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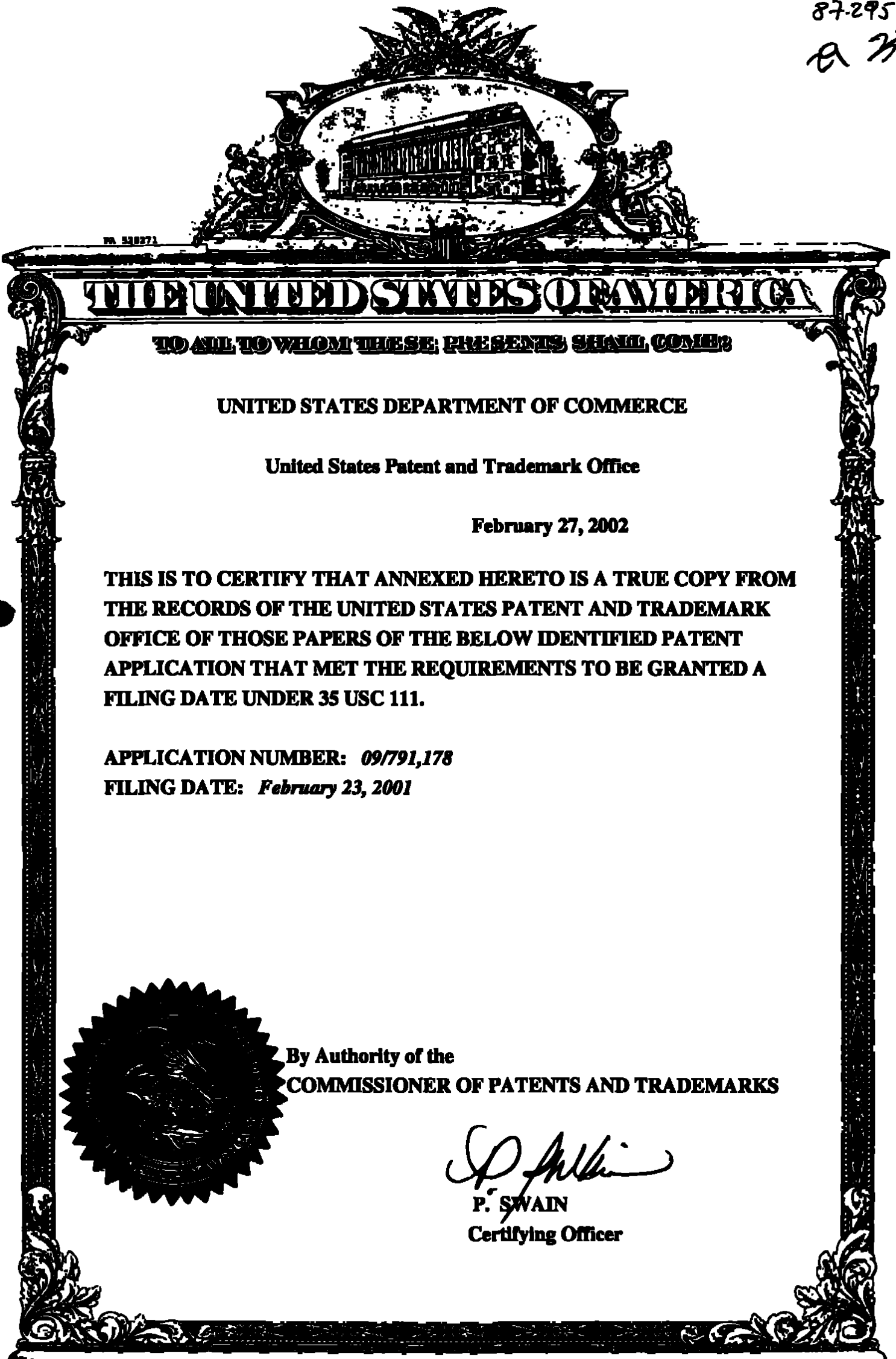
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PTO/USPS (7-03)
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UTILITY PATENT APPLICATION TRANSMITTAL

Attorney Docket No. 00-600
First Inventor Douglas Espin et al.
Title METHOD FOR REMOVING H₂S AND CO₂ FROM CRUDE OIL GAS STREAMS
Express Mail Label No. FI 394338019115

(Only for new nonprovisional applications under 37 CFR 1.53(b))

APPLICATION ELEMENTS

See MPEP chapter 800 concerning utility patent application elements.

1. ☒ Fee Transmittal Form (e.g., PTO/USPS 17)
(Submit as original unless duplicate for fee payment)
2. ☐ Applicant claims small entity status.
See 37 CFR 1.27.
3. ☒ Specification (Total Pages 18)
(Include amendment and fee if any)
- Descriptive title of the invention
- Cross Reference to Related Applications
- Statement Regarding Fed sponsored R & D
- Reference to sequence listing, a table, or a computer program listing appendix
- Background of the invention
- Brief Summary of the invention
- Brief Description of the Drawings (if any)
- Detailed Description
- Claims(s)
- Abstract of the Disclosure
4. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets 1]
5. ☒ Oath or Declaration [Total Pages 7]
a. ☒ Newly executed (original or copy)
Copy from a prior application (37 CFR 1.53 (ii))
(for continuation-in-part with Ser 78 completed)
b. ☐ DELETION OF INVENTOR(S)
(Signed statement attesting deletion of inventor(s) named in the prior application, see 37 CFR 1.53(d)(2) and 1.58(d))
6. ☐ Application Data Sheet. See 37 CFR 1.76

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7. ☐ CD-ROM or CD-R in duplicate, large table or Computer Program (Appendix)
8. ☐ Nucleotide under Amino Acid Sequence Submission (if applicable, of necessity)
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b. ☐ Specification Sequence Listing etc.
i. ☐ CD-ROM or CD-R (2 copies); or
ii. ☐ paper
c. ☐ Statements verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

9. ☒ Assignment Papers (cover sheet & document(s))
10. ☐ 37 CFR 3.730(a) Statement (when there is an assignment) ☐ Power of Attorney
11. ☐ English Translation Document (if applicable)
12. ☐ Information Disclosure Statement (IDS)/PTO-1449 ☐ Copies of IDS Claims
13. ☐ Preliminary Amendment
14. ☒ Return Receipt Postcard (MPEP 802) (should be specifically limited)
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16. ☐ Request and Certification under 35 U.S.C. 122 (b)(2)(B)(i). Applicant must attach form PTO/USPS or its equivalent.
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18. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment, or in an Application Data Sheet under 37 CFR 1.76:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP)

of prior application No. _____

Prior application Information:

Number _____

Serial No. _____

For CONTINUATION OR DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under this title, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been specifically certified from the submitted application paper.

19. CORRESPONDENCE ADDRESS

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FEE TRANSMITTAL for FY 2001

Patent fees are subject to annual revision

TOTAL AMOUNT OF PAYMENT	(3) 750.00
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Complete If Known

Application Number	
Filing Date	
First Named Inventor	Douglas Espin et al.
Examiner Name	
Group Art Unit	
Attorney Contact No.	00-600

METHOD OF PAYMENT

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~~and all~~ such agreements as:

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☐ **Applicant claims small entity status. See 37 CFR 1.55**

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FEE CALCULATION

1. BASIC FILING FEE

Large Utility Small Utility	Fee	Fee	Fee	Fee	Fee Description
Code (0)	Code (0)	Code (0)	Code (0)		
101	710	201	305		Utility Wiring Fee
105	320	206	100		Design Wiring Fee
107	400	207	245		Plant Wiring Fee
108	710	208	305		Telephone Wiring Fee
114	180	214	75		Predefined Wiring Fee

SUBTOTAL 10 710.00

2. EXTRA CLAW FEED

	Total Claims	Independent Claims	Multistate Discounted	State Claims	Fees from State	Fees Paid
	16	- 90% =	- 90% =	X		
				X		

Large Saddle		Small Saddle		Fee Description
Fee Code	Fee (\$)	Fee Code	Fee (\$)	
103	10	203	0	Chairs in excess of 20
102	20	202	40	Independent chairs in excess of 3
104	270	204	100	Multiple dependent chairs, if not paid
105	80	205	40	** Refuse independent chairs over original permit
110	10	210	0	** Refuse chairs in excess of 20 and/or other subject request

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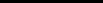
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FIRE CALCULATION (continued)

Fees				Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code (\$)	Fee (\$)		
106	130	285	85	Surcharge - late filing fee or oath	
127	85	237	25	Surcharge - late procedural filing fee or cover sheet	
138	138	138	138	Non-English specification	
147	2,830	147	2,830	Per filing a request for oral prior examination	
113	830*	113	830*	Requesting publication of SRI prior to substantive action	
113	1,840*	113	1,840*	Requesting publication of SRI after substantive action	
116	110	315	88	Extension for reply within first month	
116	300	315	188	Extension for reply within second month	
117	800	317	448	Extension for reply within third month	
118	1,300	318	888	Extension for reply within fourth month	
120	1,800	320	948	Extension for reply within fifth month	
110	310	310	168	Notice of Appeal	
120	310	320	188	Filing a brief in support of an appeal	
121	270	281	188	Request for oral hearing	
130	1,910	130	1,910	Petition to institute a public use proceeding	
140	110	340	88	Petition to revive - unavailable	
141	1,340	341	820	Petition to revive - unintentional	
142	1,340	342	820	Utility issue fee (for requests)	
143	440	343	220	Design issue fee	
144	800	344	300	Plant issue fee	
123	130	123	130	Petitions to the Commissioner	
123	130	123	130	Petitions related to procedural applications	
136	180	136	180	Submission of Information Checksheet Sheet	
591	45	591	45	Rescinding each patent assignment per property (divine number of properties)	40.00
148	710	348	388	Filing a submission after final rejection (37 CFR § 1.120(c))	
148	710	348	388	For each additional invention to be examined (37 CFR § 1.120(d))	
170	710	370	388	Request for Continued Examination (RCE)	
188	800	188	800	Request for expedited examination of a division application	

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QUESTIONS

Name (Print)	Gregory P. LaPorte
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Telephone	203-777-6628
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February 23, 2001

Panel 1

Rachel Piscitelli

Rachel Carson
February 23, 2000

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APPLICATION FOR LETTERS PATENT

TO WHOM IT MAY CONCERN:

BE IT KNOWN THAT, DOUGLAS ESPIN, AARON RANSON and
 MARIELA ARAUJO, citizens and residents of Venezuela, have
 invented certain new and useful improvements in METHOD FOR
 REMOVING H₂S AND CO₂ FROM CRUDE AND GAS STREAMS of which the
 following is a specification.

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February 23, 2001

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 February 23, 2001
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33BACKGROUND OF THE INVENTION

The present invention relates to a method for removing H_2S and CO_2 from crude and gas streams.

A long standing problem in the oil and gas industry is the presence of H_2S or hydrogen sulfide gas in hydrocarbons. H_2S must frequently be removed before a hydrocarbon can be further processed and/or used as a commercial product.

Another routinely encountered contaminant is CO_2 , which frequently must be removed as well.

Various surface scrubbing methods and H_2S or CO_2 removal devices and methods are known, but the need remains for a simple and efficient method for removal of contaminants in a downhole environment as well as at the surface.

It is therefore the primary object of the present invention to provide a method for removing H_2S and/or CO_2 from hydrocarbon gas and crude streams.

It is a further object of the present invention to provide a method for removal of H_2S which is simple and economic in use, and friendly to the environment.

Other objects and advantages of the present invention will appear hereinbelow.

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SUMMARY OF THE INVENTION

In accordance with the present invention, the foregoing objects and advantages have been readily attained.

According to the invention, a method is provided for removing at least one contaminant selected from the group consisting of H_2S and CO_2 from hydrocarbon streams, which method comprises the steps of providing a stream of hydrocarbon containing said at least one contaminant; and positioning metal-containing nanoparticles in said stream, said metal-containing nanoparticles being selected from the group consisting of metal oxides, metal hydroxides and combinations thereof, whereby said nanoparticles adsorb said at least one contaminant from said stream.

In accordance with a preferred embodiment of the present invention, the hydrocarbon stream to be treated is a downhole stream established from a hydrocarbon producing subterranean formation to a hydrocarbon producing well, and the nanoparticles are positioned in fractures induced into the formation in the form of proppants and/or additives to proppants, whereby the hydrocarbon stream produced through the fractures is exposed to the nanoparticles and H_2S and/or CO_2 are adsorbed downhole.

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In accordance with another preferred embodiment of the present invention, the contaminant-adsorptive nanoparticles of the present invention can be utilized at surface locations as well, for example in packing filters and the like, so as to advantageously adsorb H_2S and CO_2 contaminants from hydrocarbon streams.

BRIEF DESCRIPTION OF THE DRAWINGS

A detailed description of preferred embodiments of the present invention follows, with reference to the attached drawings, wherein:

Figure 1 illustrates a preferred embodiment of the present invention wherein a fracturing fluid is injected into a well to form fractures and nanoparticles are disposed therein;

Figure 2 further illustrates the embodiment of Figure 1, wherein particles within fractures are positioned in a stream of hydrocarbon flowing from a formation into a production well;

Figure 3 illustrates an alternative embodiment of the present invention wherein a hydrocarbon stream is treated using a schematically illustrated filter pack, for example at a surface location.

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36DETAILED DESCRIPTION

The present invention relates to a method for removing H₂S and CO₂ from hydrocarbon streams, and advantageously provides for positioning of H₂S adsorptive metal-containing oxide nanoparticles within the stream at desirable locations whereby H₂S and/or CO₂ are absorbed so as to produce a hydrocarbon stream having reduced H₂S content.

In accordance with the present invention, it has been found that reactive nanoparticles having high surface area provide for excellent adsorption of H₂S and CO₂ from crude and gas hydrocarbon streams, and the adsorption capacity of such particles is not substantially adversely affected by increased temperatures. This is particularly surprising in that many conventional systems for removal of H₂S are rendered less effective in the presence of CO₂, wherein the nanoparticles of the present invention have been found to be effective at removal of both H₂S and CO₂. This finding advantageously allows for such metal oxide nanoparticles to be disposed in downhole locations whereby H₂S and CO₂ removal can be accomplished in the well as the hydrocarbon stream is being produced.

In accordance with a particularly preferred embodiment of the present invention, the reactive metal-containing nanoparticles are preferably selected from the group

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consisting of metal oxides and metal hydroxides, and mixtures thereof. These nanoparticles are useful at both surface and downhole locations, and downhole applications are particularly advantageous environments of use. For use in a downhole location, a fracturing fluid can be introduced into a well so as to form fractures in the hydrocarbon-producing formation, and the nanoparticles are then disposed in such fractures, either as propants and/or as an additive or coating to a propanant, whereby hydrocarbon streams produced through the fracture are exposed to the nanoparticles as desired.

In accordance with the present invention, suitable nanoparticles preferably have a particle size of less than or equal to about 100 nm, preferably less than or equal to about 30 nm, more preferably between about 1 nm and about 20 nm and most preferably between about 1 nm and about 10 nm. These nanoparticles can be produced utilizing any known techniques. Examples of disclosures related to preparation of suitable nanoparticles are presented in U.S. Patent Nos. 5,759,939, 4,977,647 and 6,087,294.

It is preferred that the nanoparticles of the present invention have a surface area greater than or equal to about 80 m²/g, which has been found to provide excellent

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adsorption capacity as will be demonstrated in the examples which follow.

Suitable materials from which nanoparticles can be provided in accordance with the present invention include metal oxides and/or metal hydroxides, and the metal is preferably a metal selected from the group consisting of calcium, magnesium, zinc, iron and other metals from groups 8, 9 or 10 or the periodic table of elements (CAS Group VIII). For adsorption of H_2S , the most preferred material is calcium oxide (CaO), and for adsorption of CO_2 , the most preferred material is calcium oxide coated with iron oxide ($[Fe_2O_3]CaO$). For environments where both H_2S and CO_2 are to be removed and CO_2 is present in amounts of greater than 50% by vol., the most preferable nanoparticles have been found to be calcium oxide coated with iron oxide ($[Fe_2O_3]CaO$).

It is particularly preferred that nanoparticles in accordance with the present invention have a chemical structure containing less than or equal to about 100 atoms. This advantageously provides for increased surface area and adsorption of H_2S and CO_2 even in the presence of other gases, all as desired in accordance with the present invention.

As set forth above, nanoparticles in accordance with the present invention are positioned in an H_2S and/or CO_2 -

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containing hydrocarbon stream, and the nanoparticles serve to adsorb the H_2S/CO_2 from the hydrocarbon stream so as to provide a hydrocarbon product having reduced H_2S content.

The nanoparticles in accordance with the present invention can be positioned within a stream of hydrocarbon to be treated in a number of different ways. It is within the broad scope of the present invention to position the nanoparticles in various packed filters, which can be made from nanoparticle pellets or powder packing, and such filters can be positioned at the surface of a well and/or downhole through a production tubing, or in any other desired location. In accordance with a particularly preferred embodiment of the present invention, in wells which are to be fractured for enhancing production, nanoparticles are disposed in the fractures for contacting fluid as it flows into the well.

In the downhole fracture environment, nanoparticles may suitably be disposed within the fractures by fracturing the formation with a fracturing fluid and following the fracturing fluid with a fluid carrying the nanoparticles. Flowing of this fluid through the formed fractures disposes the nanoparticles therein and serves to stabilize such fractures as desired, and further position the desired high surface area metal-containing nanoparticles within the

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hydrocarbon stream to be produced through such fractures, all as desired in accordance with the present invention.

Referring to Figure 1, this preferred embodiment is schematically illustrated. Figure 1 shows a well 10 positioned to a subterranean hydrocarbon producing formation 12 and having perforations 14 through which hydrocarbons are produced. A fracturing fluid 15 is injected into well 10 and reaches formation 12 through perforations 14 at pressure and flow rate sufficient to form fractures 18 within formation 12. Fluid 16 carrying nanoparticles in accordance with the present invention is then pumped into well 10, and the nanoparticles are positioned within fractures 18 as schematically illustrated in Figure 1 and as desired in accordance with the present invention.

It is conventional in fracturing processes to include various propan particles in the fracturing fluid, or in a wash after the fracturing fluid, so that such propan particles are positioned within the fractures to hold such fractures open and enhance flow through same. In accordance with the present invention, the reactive metal oxide nanoparticles may themselves be used as propan particles, or such nanoparticles can be disposed as a

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coating or other ingredient or additive to the propants, so as to provide the desired positioning within fractures 18.

In accordance with the present invention, the metal-containing nanoparticles may be utilized in various forms. The most preferred form is to agglomerate these nanoparticles into pellets of suitable size and dispose such pellets into the hydrocarbon stream. Alternatively, if desired, the nanoparticles may be disposed onto other substrate particles and the like, if desired.

It should be noted that Figure 1 illustrates a well 10 having perforations 14. The method and nanoparticles of the present invention would also be applicable for open hole wells and any other environment for downhole or surface application.

Figure 2 shows the well 10 of Figure 1 after the fracturing step has been carried out and schematically shows hydrocarbon 20 being produced from fractures 18 into well 10 and flowing past particles within fracture 18, such that product 22 has reduced H₂S and CO₂ content.

In accordance with the present invention, it has been found that suitable metal-containing nanoparticles have substantially larger adsorption capacity than any conventional product, and that this H₂S adsorption capacity is not adversely affected by the presence of other gases

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such as CO₂, or by increased temperature, and CO₂ can in fact be removed as well. As set forth above, the resistance to increased temperature makes the nanoparticles of the present invention particularly well suited to downhole application as illustrated in Figures 1 and 2.

Depending upon the flow to which nanoparticles in accordance with the present invention are exposed, nanoparticles will have a useful lifetime of approximately two years. Of course, nanoparticles can readily be replaced in the form of different filter packs, and/or during other service operations on the well.

Turning to Figure 3, an alternative application of nanoparticles in accordance with the present invention is illustrated. As schematically shown, nanoparticles can be disposed within a filter pack 24 and positioned along a flow of hydrocarbon to be treated. Figure 3 schematically shows a stream 26 containing H₂S and CO₂ being fed to filter pack 24, and a product stream 28 having reduced H₂S and CO₂ content as desired in accordance with the present invention. Such a filter pack 24 can advantageously be positioned at any desired location along a hydrocarbon stream carrying hydrocarbons to be treated.

It is noted that the embodiments of Figures 1-3 all advantageously serve to provide excellent reduction in H₂S

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and CO₂ content in the hydrocarbon stream, and show enhanced removal-capacity as compared to commercial products.

Further, the particular characteristics of nanoparticles in accordance with the present invention allow for the downhole application of such nanoparticles, and thereby the downhole removal of H₂S and CO₂, which provides a significant benefit in the industry.

It has also been found that the process by-products are environmentally friendly metal sulfates which can be used in other applications and industries, for example as a fertilizer for agriculture and soil enrichment, and in the fabrication of cement for construction applications. Thus, the metal oxide nanoparticles and method for using same in accordance with the present invention also provide an environmentally friendly method for disposition of the H₂S and CO₂.

EXAMPLE 1

A number of different metal oxide compounds were evaluated to identify the typical surface area thereof, and this information is set forth in Table 1 below.

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Table 1

Compound	Typical Surface Area (m ² /g)	Compound	Typical Surface Area (m ² /g)
AP-MgO	400	AP-CaO	130
CP-MgO	200	CP-CaO	100
CM-MgO	10-30	CM-CaO	1-3

The compounds evaluated were three different types of magnesium oxide and three different types of calcium oxide. The three types of magnesium oxide were AP-MgO, CP-MgO, and CM-MgO. AP-MgO is magnesium oxide prepared according to an aerogel process, which is a non-evaporative process for forming nanoparticles. The CP-MgO is magnesium oxide formed according to conventional nanoparticles-forming processes, and the CM-MgO is commercially available magnesium oxide. The AP, CP and CM denominations have the same meaning for the calcium oxide particles as well.

The compositions of Table 1, as well as iron oxide-coated calcium oxide Fe₂O₃(CaO)-AP were evaluated at 40°C and at 120°C for adsorption capacity in terms of adsorption capacity (pounds of gas removed per pound of product), as were one commercial H₂S product bearing the trademark SULFATREAT™, from Sulfatreat Company.

Table 2 below sets forth the results in terms of adsorption capacity (lb/lb) for each oxide.

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Table 2

Ads	Temp	Gas	Ads. Cap. (lb. gas rem/lb. product)
CaO-CP	40°C	H ₂ S	0.628
CaO-CP	120°C	H ₂ S	0.54
Fe ₂ O ₃ (CaO) (AP)	40°C	H ₂ S	0.43
Fe ₂ O ₃ (CaO) (AP)	120°C	H ₂ S	0.37
MgO-AP	40°C	H ₂ S	0.19
Sulfatreat	40°C	H ₂ S	0.12
CaO-CP	40°C	CO ₂	0.41
[Fe ₂ O ₃] CaO	40°C	CO ₂	0.56
Ca (OH) ₂	40°C	H ₂ S	0.48
ZnO	40°C	H ₂ S	0.38
ZnO	120°C	H ₂ S	0.43

It should be readily appreciated that a method has been provided in accordance with the present invention which advantageously meets the objective set forth herein, and which is particularly useful in removal of H₂S from hydrocarbon streams at surface or downhole locations.

It is to be understood that the invention is not limited to the illustrations described and shown herein, which are deemed to be merely illustrative of the best modes of carrying out the invention, and which are susceptible of modification of form, size, arrangement of parts and details of operation. The invention rather is intended to encompass all such modifications which are within its spirit and scope as defined by the claims.

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46WHAT IS CLAIMED IS:

1. A method for removing at least one contaminant selected from the group consisting of H_2S and CO_2 from hydrocarbon streams, comprising the steps of:

providing a stream of hydrocarbon containing said at least one contaminant; and

positioning metal-containing nanoparticles in said stream, said metal-containing nanoparticles being selected from the group consisting of metal oxides, metal hydroxides and combinations thereof, whereby said nanoparticles adsorb said at least one contaminant from said stream.

2. The method of claim 1, wherein said stream is established from a hydrocarbon producing subterranean formation to a hydrocarbon producing well, and further comprising the steps of forming fractures in said formation and positioning said nanoparticles in said fractures.

3. The method of claim 2, wherein said forming step comprises injecting a fracturing fluid through said well into said formation, and following said fracturing fluid with a fluid carrying said nanoparticles whereby said nanoparticles are positioned in said fractures.

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4. The method of claim 1, wherein said nanoparticles have a particle size of less than or equal to about 100 nm.

5. The method of claim 1, wherein said nanoparticles have a particle size of less than or equal to about 30 nm.

6. The method of claim 1, wherein said nanoparticles have a particle size of between about 1 nm and about 20 nm.

7. The method of claim 1, wherein said nanoparticles have a particle size of between about 1 nm and about 10 nm.

8. The method of claim 1, wherein said nanoparticles have a surface area of at least about 80 m²/g.

9. The method of claim 1, wherein said hydrocarbon stream is selected from the group consisting of hydrocarbon gas, crude and mixtures thereof.

10. The method of claim 1, wherein said nanoparticles contain a metal selected from the group consisting of calcium, magnesium, zinc, iron, and metals from groups 8, 9

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and 10 of the period table of elements, and combinations thereof.

11. The method of claim 1, wherein said nanoparticles are calcium oxide having a surface area of greater than or equal to about 80 m²/g.

12. The method of claim 1, wherein said hydrocarbon stream contains H₂S and CO₂, and said nanoparticles are iron oxide-coated calcium oxide particles.

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ABSTRACT

A method for removing at least one contaminant selected from the group consisting of H_2S and CO_2 from hydrocarbon streams, including the steps of providing a stream of hydrocarbon containing the at least one contaminant; the positioning metal-containing nanoparticles in the stream, the metal-containing nanoparticles being selected from the group consisting of metal oxides, metal hydroxides and combinations thereof, whereby the nanoparticles adsorb the contaminants from the stream.

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Practitioner's Docket No. 00-600

PATENT

COMBINED DECLARATION AND POWER OF ATTORNEY
(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL, CONTINUATION, OR C-I-P)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type:

(check one applicable item below)

☒ original.

☐ design.

NOTE: With the exception of a supplemental oath or declaration submitted in a reissue, a supplemental oath or declaration is not treated as an amendment under 37 CFR 1.512 (Amendments after allowance), M.P.E.P. § 714.16, 7th Edition.

☐ supplemental.

NOTE: If the declaration is for an international Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.

☐ national stage of PCT.

NOTE: If one of the following 3 items apply, then complete and also attach **ADDED PAGES FOR DIVISIONAL, CONTINUATION OR C-I-P**.

NOTE: See 37 C.F.R. § 1.634 (continued prosecution application) for use of a prior nonprovisional application declaration in the continuation or divisional application being filed on behalf of the same or fewer of the inventors named in the prior application.

☐ divisional.

☐ continuation.

NOTE: Where an application discloses and claims subject matter not disclosed in the prior application, or a continuation or divisional application names an inventor not named in the prior application, a continuation-in-part application must be filed under 37 C.F.R. § 1.634 (application filing requirements — nonprovisional application).

☐ continuation-in-part (C-I-P).

INVENTORSHIP IDENTIFICATION

WARNING: If the inventors are each not the inventors of all the claims, an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.

My residence, post office address and citizenship are as stated below, next to my name. I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter that is claimed, and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

METHOD FOR REMOVING H₂S FROM CRUDE AND GAS STREAMS

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51 SA 51 09791178.022301 SPECIFICATION IDENTIFICATION

the specification of which:

(complete (a), (b), or (c))

(a) ☒ is attached hereto.

NOTE: "The following combinations of information supplied in an oath or declaration filed on the application filing date with a specification are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.82:

"(1) name of inventor(s), and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration on filing;

"(2) name of inventor(s), and attorney docket number which was on the specification as filed;

or

"(3) name of inventor(s), and title which was on the specification as filed."

Notice of July 13, 1986 (1177 O.G. 82).

(b) ☐ was filed on _____, as ☐ Serial No. 0 / _____
or ☐ _____
and was amended on _____ (if applicable).

NOTE: Amendments filed after the original papers are deposited with the PTO that contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 C.F.R. § 1.87.

NOTE: "The following combinations of information supplied in an oath or declaration filed after the filing date are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 CFR 1.82:

"(4) application number (consisting of the series code and the serial number, e.g., 08/123,456);

"(5) serial number and filing date;

"(6) attorney docket number which was on the specification as filed;

"(7) title which was on the specification as filed and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration; or

"(8) title which was on the specification as filed and accompanied by a cover letter accurately identifying the application for which it was intended by either the application number (consisting of the series code and the serial number, e.g., 08/123,456), or serial number and filing date. Absent any statement(s) to the contrary, it will be presumed that the application filed in the PTO is the application which the inventor(s) executed by signing the oath or declaration."

M.P.E.P. § 801.01(a), 7th Ed.

(c) ☐ was described and claimed in PCT International Application No. _____, filed on _____ and as amended under PCT Article 19 on _____ (if any).

(Declaration and Power of Attorney [1-1]—page 2 of 7)

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SUPPLEMENTAL DECLARATION (37 C.F.R. § 1.57(b))

(complete the following where a supplemental declaration is being submitted)

☒ I hereby declare that the subject matter of the

☐ attached amendment

☐ amendment filed on _____

was part of my/our invention and was invented before the filing date of the original application, above-identified, for such invention.

ACKNOWLEDGEMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, § 1.56,

(also check the following items, if desired)

☒ and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent, and

☐ In compliance with this duty, there is attached an information disclosure statement, in accordance with 37 C.F.R. § 1.88.

PRIORITY CLAIM (35 U.S.C. §§ 110(a)-(d))

NOTE: "The claim to priority need be in no special form and may be made by the attorney or agent if the foreign application is referred to in the oath or declaration as required by § 1.53. The claim for priority and the certified copy of the foreign application specified in 35 U.S.C. 110(a) must be filed in the case of an interference (§ 1.632), when necessary to overcome the date of a reference relied upon by the examiner, when specifically required by the examiner, and in all other situations, before the patent is granted. If the claim for priority or the certified copy of the foreign application is filed after the date the issue fee is paid, it must be accompanied by a petition requesting entry and by the fee set forth in § 1.17(b). If the certified copy is not in the English language, a translation need not be filed except in the case of interference; or when necessary to overcome the date of a reference relied upon by the examiner; or when specifically required by the examiner, in which event an English language translation must be filed together with a statement that the translation of the certified copy is accurate." 37 C.F.R. § 1.55(d).

I hereby claim foreign priority benefits under Title 35, United States Code, §§ 110(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (c) or (a))

(c) ☒ no such applications have been filed.

(a) ☐ such applications have been filed as follows.

NOTE: Where item (a) is entered above and the international Application which designated the U.S. itself claimed priority check item (a), enter the details below and make the priority claim.

(Declaration and Power of Attorney [1-1]-page 3 of 7)

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**PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION
AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119(a)-(d)**

COUNTRY (OR INDICATE IF PCT)	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 37 USC 119
			☐ YES ☐ NO
			☐ YES ☐ NO
			☐ YES ☐ NO
			☐ YES ☐ NO
			☐ YES ☐ NO

**CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)
(34 U.S.C. § 119(e))**

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

PROVISIONAL APPLICATION NUMBER

FILING DATE

_____/_____/_____
_____/_____/_____
_____/_____/_____

**CLAIM FOR BENEFIT OF EARLIER US/PCT APPLICATION(S)
UNDER 35 U.S.C. § 120**

- ☐ The claim for the benefit of any such applications are set forth in the attached ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR CONTINUATION-IN-PART (C-I-P) APPLICATION.

(Declaration and Power of Attorney [1-1]—page 4 of 7)

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**ALL FOREIGN APPLICATIONS, IF ANY, FILED MORE THAN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION**

NOTE: If the application filed more than 12 months from the filing date of this application is a PCT filing forming the basis for this application entering the United States as (1) the national stage, or (2) a continuation, divisional, or continuation-in-part, then also complete **ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR C-I-P APPLICATION** for benefit of the prior U.S. or PCT application(s) under 35 U.S.C. § 120.

POWER OF ATTORNEY

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

(Set name and registration number)

Robert H. Bachman (19,374), Gregory P. LaPointe (28,585),
Barry L. Kalmechster (29,988), and George A. Coury (34,308),
all of Bachman & LaPointe, P.C., 900 Chapel Street, Suite
1201, New Haven, CT 06510-2802

(check the following item, if applicable)

- ☒ I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.
- ☐ Attached, as part of this declaration and power of attorney, is the authorization of the above-named practitioner(s) to accept and follow instructions from my representative(s).

SEND CORRESPONDENCE TO

DIRECT TELEPHONE CALLS TO:
(Name and telephone number)

☒ Address
Bachman & LaPointe, P.C.
900 Chapel Street, Suite 1201
New Haven, CT 06510-2802

Gregory P. LaPointe
(203) 777-6628, ext. 111

☐ Customer Number _____

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DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

NOTE: Carefully indicate the family (or last) name, as it should appear on the filing receipt and all other documents.

NOTE: Each inventor must be identified by full name, including the family name, and at least one given name without abbreviation together with any other given name or initial, and by his/her residence, post office address and country of citizenship. 37 CFR § 1.53(a)(3).

NOTE: Inventors may execute separate declarations/oaths provided each declaration/oath sets forth all the inventors. Section 1.53(a)(3) requires that a declaration/oath, inter alia, identify each inventor and prohibits the execution of separate declarations/oaths which each sets forth only the name of the executing inventor. 62 Fed. Reg. 53,131, 53,142, October 10, 1997.

Full name of sole or first inventor

Douglas Espin
(GIVEN NAME) (MIDDLE INITIAL OR NAME) (FAMILY (OR LAST) NAME)
Inventor's signature [Signature]
Date February 22, 2001 Country of Citizenship Venezuela
Residence Calle Yonaco, Dtm. Canaima, Macaracay, Caracas
Post Office Address Intever, Edo. Miranda, Appo. 76343, Caracas 1070-A, Venezuela.

Full name of second joint inventor, if any

Aaron Ranson
(GIVEN NAME) (MIDDLE INITIAL OR NAME) (FAMILY (OR LAST) NAME)
Inventor's signature [Signature]
Date February 21, 2001 Country of Citizenship Venezuela
Residence Cda. Jai-Ras, La Arboleda, San Antonio, Edo. Miranda, Venezuela
Post Office Address Appo. 76343, Caracas, 1070-A, Venezuela

Full name of third joint inventor, if any

Mariela Araujo
(GIVEN NAME) (MIDDLE INITIAL OR NAME) (FAMILY (OR LAST) NAME)
Inventor's signature [Signature]
Date February 21, 2001 Country of Citizenship Venezuela
Residence Conf. Res. Trebol Hills, Apt. B-PB-C, San Antonio de los Altos
Post Office Address Intever S.A. Apartado 76343 Caracas 1070-A, Venezuela

(Declaration and Power of Attorney (1-1)—page 6 of 7)

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(check proper boxes) for any of the following added page(s)
that form a part of this declaration)

- ☐ Signature for fourth and subsequent joint inventors. Number of pages added _____

. . .

- ☐ Signature by administrator(trib), executor(trib) or legal representative for deceased or incapacitated inventor. Number of pages added _____

. . .

- ☐ Signature for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR 1.47. Number of pages added _____

. . .

- ☐ Added page for signature by one joint inventor on behalf of deceased inventor(s) where legal representative cannot be appointed in time. (37 CFR 1.47)

. . .

- ☐ Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (C-I-P) application.

☐ Number of pages added _____

. . .

- ☐ Authorization of practitioner(s) to accept and follow instructions from representative.

. . .

(If no further pages form a part of this Declaration,
then end this Declaration with this page and check the following item)

☒ This declaration ends with this page.

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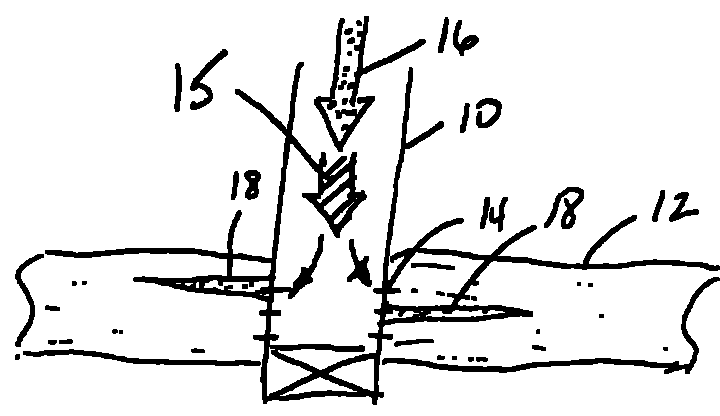


FIG. 1

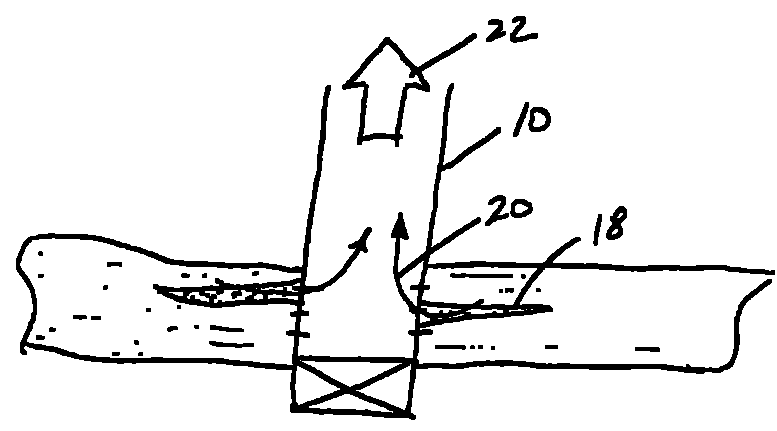


FIG. 2

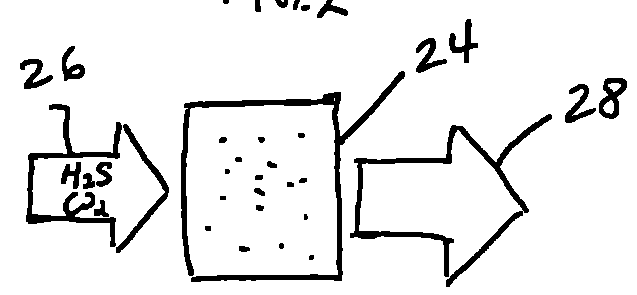


FIG. 3

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**TRADUCCIÓN DEL INGLÉS AL CASTELLANO de la Solicitud de
Patente de los Estados Unidos No.09/791,178 relacionada con:**

**MÉTODO PARA RETIRAR H₂S Y CO₂ DE CORRIENTES DE
CRUDO Y GAS.**

**ANEXOS. La Solicitud de Patente de los Estados Unidos Serie No.09/
791,178 arriba mencionada, Declaración y Poder, Solicitud de Patente,
Certificación del Comisionado de Patentes y Marcas de los Estados
Unidos de América.**

LOS ESTADOS UNIDOS DE AMÉRICA

**DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS DE
AMÉRICA**

Oficina de Patentes y Marcas de los Estados Unidos

Febrero 27, 2002

**ESTE PARA CERTIFICAR QUE ANEXO AL PRESENTE SE
ENCUENTRA UNA FIEL COPIA TOMADA DE LOS REGISTROS
DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS
UNIDOS DE AQUELLOS DOCUMENTOS DE LA SOLICITUD DE
PATENTE IDENTIFICADA ABAJO LA CUAL CUMPLE LOS
REQUISITOS PARA CONCEDERLE UNA FECHA DE
PRESENTACIÓN BAJO LA NORMA 35USC 111.**

**NUMERO DE SOLICITUD: 09/791,178
FECHA DE PRESENTACION: Febrero 23, 2001**

**Por autorización del .
COMISIONADO DE PATENTES Y MARCAS
P. Swain (Firmado)
P. SWAIN
Funcionario de Certificaciones**

SELLO ADHERIDO

00-600

ANTECEDENTES DE LA INVENCION

**La presente invención se relaciona con un método para retirar H₂S
y CO₂ de corrientes de crudo y gas.**

Un problema de larga duración en la industria del petróleo y gas es la presencia de H_2S o sulfuro de hidrógeno en hidrocarburos. El H_2S debe retirarse frecuentemente antes de que un hidrocarburo pueda procesarse adicionalmente y/o sea utilizado como un producto comercial.

Otro contaminante encontrado rutinariamente es el CO_2 , el cual frecuentemente debe retirarse igualmente.

Varios métodos de restregar superficies y dispositivos y métodos de retiro de H_2S o CO_2 se conocen, pero permanece la necesidad de un método simple y eficiente para el retiro de contaminantes en un ambiente de barreno así como en la superficie.

Consecuentemente es un objetivo primario de la presente invención proporcionar un método para retirar H_2S y/o CO_2 de corrientes de gas hidrocarburo y crudo.

Es un objetivo adicional de la presente invención proporcionar un método para retiro de H_2S que sea simple y económico en el uso, y amistoso para el ambiente.

Otros objetivos y ventajas de la presente invención aparecerán enseguida.

RESUMEN DE LA INVENCION

De acuerdo con la presente invención, los anteriores objetivos y ventajas se lograrán fácilmente.

De acuerdo con la invención, se proporciona un método para retirar por lo menos un contaminante seleccionado a partir del grupo que consiste de H_2S y CO_2 de corrientes de hidrocarburo, cuyo método comprende los pasos de proporcionar una corriente de hidrocarburo que contiene dicho por lo menos un contaminante; y colocar nanopartículas que contienen el metal en dicha corriente, dichas nanopartículas que contienen el metal seleccionadas a partir del grupo que consiste de óxidos de metal, hidróxidos de metal, sus combinaciones, por lo cual dichas nanopartículas adsorben dicho por lo menos un contaminante de dicha corriente.

De acuerdo con una modalidad preferida de la presente invención, la corriente de hidrocarburo a ser tratada es una corriente de barreno establecida de una formación subterránea que produce hidrocarburo a un pozo de producción de hidrocarburo, y las nanopartículas son colocadas en fracturas inducidas dentro de la formación en forma de propulsores

y/o aditivos a propulsores, por lo cual la corriente de hidrocarburos producida a través de las fracturas es expuesta a las nanopartículas y el H_2S y/o CO_2 son adsorbidos en el barreno.

De acuerdo con otra modalidad preferida de la presente invención, las nanopartículas adsorbtivas de contaminantes de la presente invención pueden utilizarse en localizaciones superficiales igualmente, por ejemplo en filtros de paquete y similares, en forma tal de adsorber ventajosamente contaminantes de H_2S y CO_2 de corrientes de hidrocarburos.

BREVE DESCRIPCIÓN DE LOS DIBUJOS

Enseguida se encuentra una descripción detallada de las modalidades preferidas de la presente invención, con referencia a los dibujos anexos, donde:

La Figura 1 ilustra una modalidad preferida de la presente invención, donde un fluido de fracturado es inyectado dentro de un pozo para formar fracturas y nanopartículas se colocan allí;

la Figura 2 ilustra adicionalmente la modalidad de la Figura 1, donde las partículas dentro de las fracturas están colocadas en una corriente de hidrocarburos que fluye desde una formación dentro de un pozo de producción;

la Figura 3 ilustra una modalidad alternativa de la presente invención donde una corriente de hidrocarburos se trata utilizando un paquete de filtro ilustrado esquemáticamente, por ejemplo en una localización superficial.

DESCRIPCIÓN DETALLADA

La presente invención se relaciona con un método para retirar H_2S y CO_2 de corrientes de hidrocarburos, y proporciona ventajosamente la colocación de nanopartículas de óxido que contienen metal adsorbtivo H_2S dentro de la corriente en las localizaciones deseables por lo cual el H_2S y/o CO_2 es absorbido en forma tal de producir una corriente de hidrocarburos que tiene contenido reducido de H_2S .

De acuerdo con la presente invención, se ha encontrado que nanopartículas reactivas que tienen alta área superficial proporcionan excelente adsorción de H_2S y CO_2 a partir de corrientes de crudo e hidrocarburo, y la capacidad de adsorción de dichas partículas no se ve sustancialmente afectada adversamente por temperaturas incrementadas. Esto es particularmente sorprendente en cuanto a que muchos sistemas convencionales para retiro de H_2S se vuelven menos efectivos en presencia de CO_2 , donde se ha encontrado que las nanopartículas de la presente invención son efectivas para el retiro tanto de H_2S como de CO_2 .

Este hallazgo permite ventajosamente que dichas nanopartículas de óxido de metal sean colocadas en localizaciones de barrenos, por lo cual el retiro de H_2S y CO_2 puede llevarse a cabo en el pozo a medida que se está produciendo la corriente de hidrocarburos.

De acuerdo con una modalidad particularmente preferida de la presente invención, las nanopartículas que contienen metal reactivo se seleccionan preferiblemente a partir del grupo que consiste de óxidos de metal e hidróxidos de metal, y sus mezclas. Estas nanopartículas son útiles tanto en localizaciones de superficie como de barrenos, y las aplicaciones de barrenos son ambientes particularmente ventajosos de uso. Para uso en localizaciones de barreno, un fluido de fracturado puede introducirse dentro del pozo en forma tal de formar fracturas en la formación de producción de hidrocarburos y las nanopartículas son colocadas entonces en dichas fracturas, ya sea como propulsores y/o como un aditivo o revestimiento para un propulsor, por lo cual las corrientes de hidrocarburo producidas a través de la fractura son expuestas a las nanopartículas como se desee.

De acuerdo con la presente invención, adecuadas nanopartículas tienen preferiblemente un tamaño de partículas menor de o igual a alrededor de 30 nm, más preferiblemente entre alrededor de 1 nm y alrededor de 20 nm y más preferiblemente aún entre alrededor de 1 nm y alrededor de 10 nm. Estas nanopartículas pueden producirse utilizando cualquier técnica conocida. Ejemplos de divulgaciones relacionadas con la preparación de adecuadas nanopartículas se presentaron en las Patentes US Nos. 5,759,939, 4,877,647 y 6,087,294.

Se prefiere que las nanopartículas de la presente invención tengan un área superficial mayor de o igual a alrededor de $80 \text{ m}^2/\text{g}$, la cual se ha encontrado que proporciona excelente capacidad de adsorción como se demostrará en los ejemplos siguientes.

Adecuados materiales a partir de los cuales pueden proporcionarse las nanopartículas de acuerdo con la presente invención incluyen óxidos de metal y/o hidróxidos de metal, y el metal es preferiblemente un metal seleccionado a partir del grupo que consiste de calcio, magnesio, zinc, hierro y otros metales de los grupos 8, 9 o 10 o la tabla periódica de elementos (CAS Grupo VIII). Para la adsorción del H_2S , el material más preferido es óxido de calcio (CaO), y para adsorción de CO_2 , el material más preferido es el óxido de calcio revestido con óxido de hierro ($[Fe_2O_3]CaO$). Para ambientes donde tanto H_2S como CO_2 se deben retirar y el CO_2 está presente en cantidades mayores de 50% en volumen, se ha encontrado que las nanopartículas más preferidas son óxido de calcio revestido con óxido de hierro ($[Fe_2O_3]CaO$).

Se prefiere particularmente que las nanopartículas de acuerdo con la presente invención tengan una estructura química que contiene menos de o igual a alrededor de 100 átomos. Esto proporciona ventajosamente una incrementada área superficial y adsorción de H_2S y CO_2 aún en presencia de otros gases, todo como se desee de acuerdo con la presente invención.

Como se estableció arriba, las nanopartículas de acuerdo con la presente invención están colocadas en un a corriente de hidrocarburos que contiene H_2S y/o CO_2 y las nanopartículas sirven para adsorber el H_2S/CO_2 de la corriente de hidrocarburos en forma tal de proporcionar un producto de hidrocarburos que tiene reducido contenido de H_2S .

Las nanopartículas de acuerdo con la presente invención pueden colocarse dentro de una corriente de hidrocarburos a ser tratada en un número de diferentes vías. Se encuentra dentro del amplio alcance de la presente invención colocar las nanopartículas en varios filtros de paquete, que pueden hacerse a partir de pellets de nanopartículas o paquetes en polvo, y dichos filtros pueden colocarse en la superficie de un pozo y/o en un barreno a través de una tubería de producción, o en cualquier otra localización deseada. De acuerdo con una modalidad particularmente preferida de la presente invención, en pozos que van a fracturarse para mejorar la producción, las nanopartículas se colocan en las fracturas para contactar el fluido a medida que fluye dentro del pozo.

En el ambiente de fractura de barreno, las nanopartículas pueden colocarse adecuadamente dentro de las fracturas fracturando la formación con un fluido de fracturado y después del fluido de fracturado con un fluido que lleva las nanopartículas. La fluencia de este fluido a través de las fracturas formadas coloca allí las nanopartículas y sirve para estabilizar dichas fracturas como se desee, y coloca adicionalmente las nanopartículas deseadas que contienen metal del alta área superficial dentro de la corriente de hidrocarburos a ser producida a través de dichas fracturas, todo tal como se desee de acuerdo con la presente invención.

Haciendo referencia a la Figura 1, esta modalidad preferida se ilustra esquemáticamente. La Figura 1 muestra un pozo 10 colocado en una formación 12 subterránea productora de hidrocarburos y que tiene perforaciones 14 a través de las cuales se producen los hidrocarburos. Un fluido de fracturado 15 es inyectado dentro del pozo 10 y alcanza la formación 12 a través de las perforaciones 14 una presión y una rata de flujo suficiente para formar las fracturas 18 dentro de la formación 12. El fluido 16 que lleva las nanopartículas de acuerdo con la presente invención se bombea entonces dentro del pozo 10, y las nanopartículas son colocadas dentro de las fracturas 18 como se ilustra en el esquema de

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la Figura 1 y como se desee de acuerdo con la presente invención.

Es convencional en procesos de fracturado incluir varias partículas propulsoras en el fluido de fracturado, o en un lavado después del fluido de fracturado en forma tal que dichas partículas propulsoras son colocadas dentro de las fracturas para mantener dichas fracturas abiertas y mejorar el flujo a su través. De acuerdo con la presente invención, las nanopartículas reactivas de óxido de metal pueden usarse ellas mismas como partículas propulsoras, o dichas nanopartículas pueden colocarse como un revestimiento u otro ingrediente o aditivo para los propulsores, en forma tal de proporcionar la deseada colocación dentro de las fracturas 18.

De acuerdo con la presente invención, las nanopartículas que contienen metal pueden utilizarse en varias formas. La forma más preferida es aglomerar esas nanopartículas en pellets de tamaño adecuado y colocar dichas pellets en la corriente de hidrocarburos. Alternativamente, si se desea, las nanopartículas pueden colocarse en otras partículas de sustrato y similares, si se desea.

Debe notarse que la Figura 1 ilustra un pozo 10 que tiene perforaciones 14. El método y las nanopartículas de la presente invención pueden ser aplicables también en pozos de orificios abiertos y cualquier otro ambiente para aplicación de barreno o de superficie.

La Figura 2 muestra el pozo 10 de la Figura 1 después de que se ha llevado a cabo el paso de fracturado y muestra esquemáticamente el hidrocarburo 20 que se produce a partir de las fracturas 18 dentro del pozo 10 y fluye pasando las partículas dentro de la fractura 18, en forma tal que el producto 22 tiene reducido contenido de H_2S y CO_2 .

De acuerdo con la presente invención, se ha encontrado que adecuadas nanopartículas que contienen metal tienen capacidad de adsorción sustancialmente mayor que cualquier producto convencional y que esta capacidad de adsorción de H_2S no se afecte adversamente debido a la presencia de otros gases tales como CO_2 o debido a la temperatura incrementada, y el CO_2 puede de hecho retirarse igualmente. Tal como se estableció arriba, la resistencia a la temperatura incrementada hace a las nanopartículas de la presente invención particularmente bien ajustadas para aplicación en barreno tal como se ilustra en las Figuras 1 y 2.

Dependiendo del flujo al cual se exponen las nanopartículas de acuerdo con la presente invención, las nanopartículas tendrán una vida útil de aproximadamente dos años. Por supuesto, las nanopartículas

pueden reemplazarse fácilmente en forma de diferentes paquetes de filtro, y/o durante otras operaciones de servicio en el pozo.

Volviendo a la Figura 3, se ilustra una aplicación alternativa de las nanopartículas de acuerdo con la presente invención. Como se muestra esquemáticamente, las nanopartículas pueden colocarse dentro de un paquete de filtro 24 y colocarse a lo largo de un flujo de hidrocarburos a ser tratado. La Figura 3 muestra esquemáticamente una corriente 26 que contiene H_2S y CO_2 alimentada al paquete de filtro 24, y una corriente de producto 28 que tiene reducido contenido de H_2S y CO_2 , como se desee, de acuerdo con la invención. Un paquete de filtro 24 tal puede colocarse ventajosamente en cualquier localización deseada a lo largo de la corriente de hidrocarburos que lleva los hidrocarburos a ser tratados.

Se anota que las modalidades de las Figuras 1 a 3 sirven todas ventajosamente para proporcionar excelente reducción en el contenido de H_2S y CO_2 en la corriente de hidrocarburos, y muestran mejorada capacidad de retiro comparado con productos comerciales. Adicionalmente, las características particulares de las nanopartículas de acuerdo con la presente invención permiten la aplicación de barreno de dichas nanopartículas, y consecuentemente el retiro de barreno de H_2S y CO_2 , lo cual proporciona un beneficio significativo en la industria.

Se ha encontrado también que los productos colaterales del proceso son sulfatos de metal ambientalmente amistosos que pueden usarse en otras aplicaciones e industrias, por ejemplo como un fertilizante para agricultura y enriquecimiento del suelo, y en la fabricación de cemento para aplicaciones en construcción. Consecuentemente, las nanopartículas de óxido de metal y el método para utilizarlas de acuerdo con la presente invención también proporcionan un método ambientalmente amistoso para el retiro de H_2S y CO_2 .

EJEMPLO 1

Un número de diferentes compuestos de óxido de metal se evaluó para identificar su área superficial típica, y esta información se establece en la Tabla 1 de abajo.

Tabla 1

Compuesto	Área superficial típica (mg^2/g)	Compuesto	Área superficial típica (mg^2/g)
AP- MgO	400	AP - CaO	130
CP - MgO	200	CP - CaO	100
CM - MgO	10 - 30	CM - CaO	1 - 3

Los compuestos evaluados fueron tres tipos diferentes de óxido de

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magnesio y tres tipos diferentes de óxido de calcio. Los tres tipos de óxido de magnesio fueron AP-MgO, CP-MgO, y CM-MgO. El AP-MgO es óxido de magnesio preparado de acuerdo con un proceso de aerogel el cual es un proceso no evaporativo para formar nanopartículas. El CP-MgO es óxido de magnesio formado de acuerdo con procesos convencionales de formación de nanopartículas, y el CM-MgO es óxido de magnesio comercialmente disponible. Las denominaciones AP, CP y CM tienen el mismo significado para las partículas de óxido de calcio igualmente.

Las composiciones de la Tabla 1, así como Fe_2O_3 (CaO)-AP óxido de hierro revestido de óxido de calcio, se evaluaron a 40°C y a 120°C en cuanto a capacidad de adsorción en términos de capacidad de adsorción (libras de gas retirado por libra de producto), como lo fue un producto comercial que lleva la marca comercial SULFATREAT®, de Sulfatreat Company.

La Tabla 2 de abajo establece los resultados en términos de capacidad de adsorción (libra/libra) para cada óxido.

Tabla 2

Ads	Temperatura °C	Gas	Capacidad de Adsorción (libra gas retirado / libra producto)
CaO-CP	40	H ₂ S	0,628
CaO-CP	120	H ₂ S	0,54
Fe ₂ O ₃ (CaO) (AP)	40	H ₂ S	0,43
Fe ₂ O ₃ (CaO) (AP)	120	H ₂ S	0,37
MgO-AP	40	H ₂ S	0,19
Sulfatreat	40	H ₂ S	0,12
CaO-CP	40	CO ₂	0,41
(Fe ₂ O ₃)CaO	40	CO ₂	0,56
Ca(OH) ₂	40	H ₂ S	0,48
ZnO	40	H ₂ S	0,38
ZnO	120	H ₂ S	0,43

Deberá apreciarse fácilmente que se ha proporcionado un método de acuerdo con la presente invención el cual cumple ventajosamente con el objetivo establecido aquí, y el cual es particularmente útil en el retiro de H₂S a partir de corrientes de hidrocarburos en localizaciones de barreno o superficiales.

Deberá entenderse que la invención no está limitada a las ilustraciones descritas y mostradas aquí, las cuales se consideran meramente ilustrativas de las mejores formas de llevar a cabo la

invención, y las cuales son susceptibles de modificación de forma, tamaño, arreglo de partes y detalles de operación. La invención pretende más bien involucrar todas las dichas modificaciones que se encuentran dentro del espíritu y alcance definido por las reivindicaciones.

REIVINDICACIONES

1. Un método para retirar por lo menos un contaminante seleccionado a partir del grupo que consiste de H_2S y CO_2 de corrientes de hidrocarburos, que comprende los pasos de:

proporcionar una corriente de hidrocarburos que contiene dicho por lo menos un contaminante; y

colocar nanopartículas que contienen metal en dicha corriente, dichas nanopartículas que contienen metal que se seleccionan a partir del grupo que consiste de óxidos de metal, hidróxidos de metal y sus combinaciones, por lo cual dichas nanopartículas adsorben dicho por lo menos un contaminante de dicha corriente.

2. El método de la reivindicación 1, donde dicha corriente se establece a partir de una formación subterránea de producción de hidrocarburos hacia un pozo de producción de hidrocarburos, y que comprende adicionalmente los pasos de formar fracturas en dicha formación y colocar dichas nanopartículas en dichas fracturas.

3. El método de la reivindicación 2, donde dicho paso de formación comprende inyectar un fluido de fracturado a través de dicho pozo dentro de dicha formación, y continuar dicho fluido de fracturado con un fluido que lleva dichas nanopartículas por lo cual dichas nanopartículas son colocadas en dichas fracturas.

4. El método de la reivindicación 1, donde dichas nanopartículas tienen un tamaño de partículas de menos de o igual a alrededor de 100 nm

5. El método de la reivindicación 1, donde dichas nanopartículas tienen un tamaño de partículas de menos de o igual a alrededor de 20 nm.

6. El método de la reivindicación 1, donde dichas nanopartículas tienen un tamaño de partículas de entre alrededor de 1 nm y alrededor de 20 nm.

7. El método de la reivindicación 1, donde dichas nanopartículas tienen un tamaño de partículas de entre alrededor de 1 nm y alrededor de 10 nm.

8. El método de la reivindicación 1, donde dichas nanopartículas tienen un área superficial de por lo menos alrededor de 80 m²/g.

9. El método de la reivindicación 1, donde dicha corriente de hidrocarburos se selecciona a partir del grupo que consiste de gas de hidrocarburos y sus mezclas.

10. El método de la reivindicación 1, donde dichas nanopartículas contienen un metal seleccionado a partir del grupo que consiste de calcio, magnesio, cinc, hierro, y metales seleccionados a partir de los grupos 8, 9 y 10 de la tabla periódica de elementos, y sus combinaciones.

11. El método de la reivindicación 1, donde dichas nanopartículas son de óxido de calcio que tienen un área superficial mayor de o igual a alrededor de 80 m²/g.

12. El método de la reivindicación 1, donde dicha corriente de hidrocarburos contiene H₂S y CO₂, y dichas nanopartículas son partículas de óxido de calcio recubiertas de óxido de hierro.

EXTRACTO

Un método para retirar por lo menos un contaminante seleccionado a partir del grupo que consiste de H₂S y CO₂ de corrientes de hidrocarburos, que incluye los pasos de proporcionar una corriente de hidrocarburos que contiene el por lo menos un contaminante; la colocación de nanopartículas que contienen metal en la corriente, las nanopartículas que contienen metal que se seleccionan a partir del grupo que consiste de óxidos de metal, hidróxidos de metal y sus combinaciones, por lo cual dichas nanopartículas adsorben los contaminantes de dicha corriente.

ES TRADUCCIÓN FIEL Y COMPLETA DEL DOCUMENTO ANEXO
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