

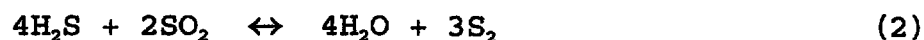
Title: Method for desulfurizing off-gases

This invention relates to a method for desulfurizing off-gases which contain a high water vapor content. More specifically, the invention comprises a method for reducing the total sulfur content of off-gases from sulfur recovery plants.

The preparation of elemental sulfur from hydrogen sulfide (H_2S) by partial oxidation thereof by means of oxygen or an oxygen-containing gas such as air, followed by reaction of the sulfur dioxide (SO_2) formed from the hydrogen sulfide, with the residual part of the hydrogen sulfide, in the presence of a catalyst, is known as the Claus process. This process is frequently employed both in refineries and for the processing of hydrogen sulfide recovered from natural gas. A conventional Claus plant consists of a burner with a combustion chamber, the so-called thermal stage, followed by a number of - generally two or three - reactors which are filled with a catalyst. These last stages constitute the so-called catalytic stages. In the combustion chamber, the incoming, H_2S -rich gas stream is combusted with an amount of air at a temperature of about $1200^\circ C$. The amount of air is set such that one-third of the H_2S is combusted to SO_2 according to the reaction:



After this partial combustion of H_2S , the unreacted part of the H_2S (i.e. about two-thirds of the amount presented) and the SO_2 formed react further for a considerable part according to the Claus reaction:



Thus, in the thermal stage, about 60% of the H_2S is converted to elemental sulfur. The gases coming from the combustion chamber are cooled to about $160^\circ C$ in a sulfur

condenser, in which the sulfur formed condenses, which subsequently flows via a siphon into a sulfur sink. The uncondensed gases, in which the molar ratio of H_2S to SO_2 is still 2 : 1, are subsequently heated to about 250°C and
5 passed through a first catalytic reactor, in which again the equilibrium $4H_2S + 2SO_2 \leftrightarrow 4H_2O + \frac{6}{n} S_n$ is established.

The gases coming from this catalytic reactor are subsequently cooled again in a sulfur condenser, whereafter the liquid sulfur formed is recovered and the residual gases,
10 after re-heating, are passed to a second catalytic reactor.

Depending on the number of catalytic stages, the sulfur recovery percentage in a conventional Claus plant amounts to 94-97%. Accordingly, an amount of H_2S and SO_2 is left.

One of the important limitations of the Claus process is
15 the increase of the water content in the process gas as the conversion of H_2S to sulfur proceeds.

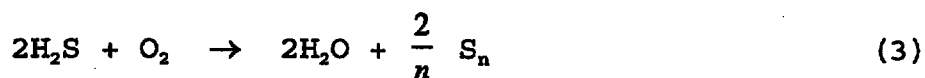
The Claus reaction is thermodynamically limited by this increase of the water vapor content and simultaneously by the decrease of the H_2S and SO_2 concentration, with the result
20 that the equilibrium of the Claus reaction (2) shifts to the left. Condensation of the water vapor in the process gas would be desirable to remove this limitation as much as possible. However, since the water dew point lies far below the solidification point of sulfur, condensation of water
25 vapor in the Claus process meets with insurmountable problems, such as clogging due to the solidification of sulfur and corrosion due to the formation of sulfurous acid.

In the past, off-gas of the Claus process was burnt in an afterburner. However, in view of the increasingly more
30 stringent environmental requirements, this is no longer permitted.

This has led to improvements of the Claus process and the development of Claus off-gas removal processes. One improvement of the Claus process is known as the SUPERCLAUS®
35 process, whereby the efficiency of the Claus process is

increased from 94-97% to more than 99%. The SUPERCLAUS[®] process is described in "SUPERCLAUS[®], the answer to Claus plant limitations", publ. 38th Canadian Chem. Eng. Conference, October 25th, 1988, Edmonton, Alberta, Canada.

5 In the SUPERCLAUS[®]-99 process, reaction (2) in the thermal stage and in the Claus reactors is operated with excess H₂S, so that in the gas from the last Claus reactor the H₂S content is approximately 1 vol.% and the SO₂ content approximately 0.02 vol.%. In a next reactor stage, the H₂S is
10 selectively oxidized to elemental sulfur according to the reaction:



15 in the presence of a special selective oxidation catalyst. These catalysts are described, for instance, in European patents 0242920 and 0409353.

As stated, increasingly more stringent environmental requirements have led not only to improvements of the Claus
20 process but also to developments of Claus tailgas processes, for the further desulfurization of off-gas from sulfur recovery plants.

Most Claus tailgas processes utilize a hydrogenation reactor, also referred to as reduction reactor, in which SO₂,
25 carbonyl sulfide (COS), carbon disulfide (CS₂), sulfur vapor and any entrained sulfur droplets (sulfur mist) are converted with hydrogen (H₂) or a reducing gas, which contains, for instance, hydrogen and carbon monoxide, to hydrogen sulfide.

The hydrogen sulfide is then removed by absorption in a
30 solution or by conversion in the gas phase to elemental sulfur, using a catalyst.

Only a few tailgas processes have been developed which, after the combustion of Claus tailgas, absorb SO₂ from chimney gas. These processes are not further discussed. Most
35 well-known among the Claus tailgas processes which, after

hydrogenation, absorb the resultant H_2S in a solution are SCOT, BSR-Stretford, BSR-MDEA, Trencor-M and Sulften. These processes are described in a publication by B.G. Goar: "Tail Gas Clean-Up Processes, a review", presented at the 33rd

- 5 Annual Gas Conditioning Conference, Norman, Oklahoma, March 7-9, 1983 and in Hydrocarbon Processing, February 1986.

The most well-known, and to date most effective, process for desulfurizing tailgas is the SCOT process described in Maddox "Gas and liquid sweetening" (1977). The SCOT process
10 achieves a sulfur recovery of 99.8 to 99.9%.

Of the tailgas processes which, after hydrogenation, convert the resultant H_2S in the gas phase using a catalyst, only a few processes have been built and become known, such as MODOP, CLINSULF, BSR-Selectox, Sulfreen, SUPERCLAUS-99.5.
15 These processes are described in the above-mentioned publication by B.G. Goar, in the journal C&EN of 11 May 1987, the journal Sulphur Jan/Feb 1995, and in DE-A 2648190.

In all these Claus tailgas processes, after the hydrogenation, the water formed in the Claus reaction (2) and
20 in the selective oxidation reaction (3) is condensed, because the presence of water has an adverse effect on the subsequent H_2S removal in an absorption liquid or in the catalytic conversion of H_2S to elemental sulfur. The absorption liquids used in the above-mentioned processes are secondary or
25 tertiary alkanolamine solutions such as Diisopropanolamine (DIPA) or Methyldiethanolamine (MDEA) or complex Redox solutions. Without removal of water, the absorption process would be thoroughly disturbed, viz., either by the too high temperatures at which no or only very slight absorption
30 occurs, or in that the water condenses in the absorber during the absorption and the circulating solution is continuously diluted, so that no absorption can take place anymore.

In H_2S conversion in the gas phase using a catalyst, without water removal the thermodynamic conversion of H_2S
35 according to the Claus reaction (2) is strongly reduced and a situation is obtained comparable to that in the last reactor

stage in the Claus process, so that a total sulfur recovery efficiency of more than 99.5% is impossible to achieve.

Although the use of a selective oxidation catalyst such as used in the SUPERCLAUS process gives a higher efficiency, with SUPERCLAUS-99.5 too, it has been found impossible in practice to achieve a sulfur recovery efficiency of more than 99.5%.

In general, it can be stated that the disadvantage of Claus tailgas processes, in which, after hydrogenation, the H_2S in the gas phase is converted to elemental sulfur using a catalyst, is that the current requirements of a total sulfur recovery efficiency of more than 99.90% cannot be met.

Claus tailgas processes with hydrogenation followed by condensation of water whereafter the H_2S is absorbed in an absorption liquid such as, for instance, in the SCOT process, can achieve total sulfur recovery efficiencies of more than 99.90%, but have as a major disadvantage that the investment costs and the energy costs are tremendously high. Newer versions of the SCOT process, such as SUPERSCOT and LS-SCOT, achieve a total sulfur recovery efficiency of 99.95%, but are even more expensive.

Another disadvantage of these processes is that acidic hydrogen sulfide-containing condensate must be discharged and treated, for instance in a Sour Water Stripper, whereby the dissolved acid gas is separated with steam. This, too, is costly.

The environmental requirements have had an influence not only on the development of Claus and Claus tailgas processes, but also on the development of chimney gas processes, also referred to as flue gas processes, for power plants. Various processes for 'flue gas desulphurization' (FGD) are known, in which SO_2 is converted with lime milk to gypsum (Ca_2SO_4). Because a surplus of gypsum has formed, processes have been searched for, in which SO_2 can be converted to elemental sulfur. The Wellman Lord process, described in Gas Purification, fourth edition 1985, A.L. Kohl, F.C.

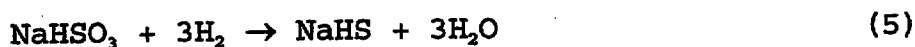
Riesenfeld, pp. 351-356, is an example, where SO₂ is eventually released as concentrated gas. After two-thirds of the SO₂ are converted to H₂S in a hydrogenation step, the H₂S and SO₂ gas can be converted to elemental sulfur in a Claus plant. This process route, too, is costly. Another development in this field is the biological desulfurization of flue gases.

Biological desulfurization of flue gases is described in the journal Lucht, number 4, December 1994. The BIO-FGD process described therein is for removing SO₂ from chimney gas from power stations and consists of an absorber where SO₂ is dissolved in a diluted sodium hydroxide solution according to the reaction



This solution is subsequently treated in two biological reactor stages.

In the first biological step, in an anaerobic reactor, the sodium bisulfite (NaHSO₃) formed is converted with an electron donor to sodium sulfide (NaHS).



Suitable electron donors are, e.g., hydrogen, ethanol, hydrogen and glucose. In the second step, in an aerobic reactor, the sodium sulfide is oxidized to elemental sulfur, which is separated.



Chimney gases contain, after combustion of coal or fuel oil, a slight amount of water vapor. The water content is typically between 2-15 vol.%, which corresponds to a water dew point of 20-55°C.

If the BIO-FGD process were used for desulfurization of Claus off-gas which has been afterburnt and whereby all sulfur components have been converted to SO₂, the gas must be cooled because of the high water vapor content of the Claus off-gas. This is done to prevent the water vapor from

condensing in the sodium hydroxide solution, as a result of which a part of the sodium hydroxide solution would constantly have to be discharged.

5 Claus off-gas must therefore be cooled, whereby sour condensate is formed and must be discharged.

In desulfurizing off-gas from a coal- or oil-fired power plant, this problem does not occur because the water dew point lies under the operating temperature in the absorber. Cooling of this off-gas can therefore be done in a simple
10 manner without the occurrence of condensation of water.

A first object of the invention is to provide a method for desulfurizing off-gases with a high water vapor content of 20 to 40 vol.% and in which condensation of this water is not necessary, thereby preventing the formation of acidic
15 hydrogen sulfide-containing condensate which must then be discharged.

A second object of the invention is to provide a method in which the H_2S formed upon hydrogenation can be absorbed in an absorption liquid at a temperature above the dew point of
20 water in the gas, so that also during the absorption of H_2S no condensation of water occurs.

A next object of the invention is to provide a method whereby a total sulfur recovery efficiency of more than 99.90% is achieved without the above-mentioned disadvantages
25 occurring.

The invention is based on the surprising insight that it is possible to absorb H_2S from such a gas with a water content of 20 to 40 vol.% at a temperature above the water dew point, in an alkaline solution, whereafter the sulfide-
30 containing solution formed is subjected to an aerobic biological oxidation.

The invention accordingly relates to a method for removing H_2S from off-gases which contain at least 20 vol.% of water vapor, comprising treating the off-gases at a
35 temperature above the water dew point of the off-gases with an aqueous, alkaline solution, under absorption of the H_2S ,

followed by subjecting the sulfide-containing solution formed to a biological oxidation of the sulfide.

Surprisingly, it has now been found that the H_2S dissolved in the alkaline solution, preferably a sodium hydroxide solution, can be oxidized to elemental sulfur with air in a biological aerobic reactor at a temperature which is preferably the same as that at which the absorption has taken place.

Such gases with a water content of 20-40 vol.% have a water dew point of 60-80°C, which means that in practice the biological oxidation will occur at a temperature of at least 65°C, more specifically at a temperature of 70 to 90°C. It is particularly surprising that it is possible to carry out an efficient and proper biological oxidation at such high temperatures.

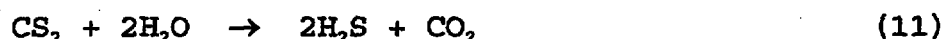
In the method according to the invention, the total sulfur content of off-gases is reduced by first raising these off-gases in temperature to a temperature above 200°C and subsequently passing them together with a hydrogen and/or carbon monoxide-containing gas over a sulfided group VI/group VIII metal catalyst on an inorganic oxidic support, whereby sulfur components such as SO_2 , sulfur vapor and sulfur mist are converted with hydrogen or another reducing gas which contains, for instance, hydrogen and carbon monoxide, to hydrogen sulfide, according to the reactions:



If oxygen is present in the off-gases, a catalyst from the above group is used which further has the property of hydrogenating oxygen according to the reaction



Preferably, a catalyst from the above group is used which further has the property of hydrolyzing COS and CS₂ according to the reactions



In the method according to the invention, the off-gases
10 from the hydrogenation reactor are cooled to just above the
dew point of the water vapor present in the gas, such that no
condensation occurs. Preferably, cooling proceeds to 3 to 5°C
above the dew point.

Off-gases, specifically off-gases from a Claus recovery
15 plant, with a water vapor content of 20 to 40 vol.%, have a
dew point between 60-80°C.

In an absorber, these off-gases are subsequently contacted directly with a diluted alkaline solution, preferably sodium hydroxide solution, with a pH between 8 and 9, whereby the H_2S present in the gas is dissolved according to the reaction:



25 The non-absorbed part of the off-gases mentioned is,
optionally after combustion, discharged to the air.

Because the regenerated alkaline solution contains no H_2S , the H_2S present in the off-gases is completely absorbed and in this manner a total sulfur recovery efficiency of more than 99.90% can be achieved. In the method according to the invention, the solution is passed to the biological aerobic reactor at the same temperature, preferably at the same temperature as that at which absorption has taken place, so that no heat needs to be removed or supplied. In the aerobic reactor an amount of air is supplied, such that the dissolved

H₂S is partially oxidized with oxygen from the air, to form elemental sulfur according to the reaction:



5

Subsequently, in a sulfur separator, preferably again at the same temperature, the sulfur is separated from the sodium hydroxide solution, whereafter the solution is recirculated to the absorber. It is possible to cool the sodium hydroxide solution having the H₂S absorbed therein before it is fed to the biological aerobic reactor. After the sulfur separation, however, the solution is then heated again before it is supplied to the absorber.

The invention will now be elucidated with reference to two figures, in which the method according to the invention is described in the form of block diagrams.

In Fig. 1 a general process diagram is represented. The off-gas of a sulfur recovery plant, not shown, is passed via line 1, with addition of hydrogen or another reducing gas via line 2, and adjusted to the desired hydrogenation temperature with heater 3, before being passed via line 4 into the hydrogenation reactor 5.

In the hydrogenation reactor 5, the sulfur dioxide, sulfur vapor and organic sulfur compounds present in the gas are converted with H₂ to H₂S. If oxygen is present in the gas, it is converted to H₂O. COS and CS₂, if present, are converted with the water vapor present, to H₂S and CO₂.

The gas from the hydrogenation reactor 5 is adjusted via line 6 to the desired absorption temperature with cooler 7, before being passed via line 8 into the absorber 9 of a bioplant. In the absorber, H₂S is washed from the gas with a diluted sodium hydroxide solution, which is subsequently passed via line 10 to an aerobic biological reactor 11, in which H₂S, with addition of oxygen from the air supplied via line 12, is converted to elemental sulfur. Via line 13 the sodium hydroxide solution is passed into a sulfur separator

14, from which the sulfur formed is discharged via line 15. The solution is recirculated via line 16 to the absorber. The gas from the absorber, which now contains only a very low content of H_2S , is passed via line 17 to the afterburner 18 before the gas is discharged via the chimney 19.

In Fig. 2 a diagram is given for a plant according to the invention, in which off-gas from a Claus plant with a high H_2S/SO_2 ratio is absorbed directly, without intermediate hydrogenation.

Off-gas coming from a three-stage Claus plant 100 is added via line 101 to absorber 102. The Claus plant 100 is operated such that the molar H_2S/SO_2 ratio is at least 100.

In the absorber 102, H_2S is washed from the gas with a diluted sodium hydroxide solution, which is subsequently passed via line 103 to an aerobic biological reactor 104, in which H_2S , with addition of oxygen from the air supplied via line 105, is converted to elemental sulfur. Via line 106, pump 107 and line 108, a portion of the sodium hydroxide solution is passed into a sulfur separator 109, from which the sulfur formed is discharged via line 110. The solution is recirculated via lines 111 and 112 to the absorber, with a small discharge via line 113. The gas from the absorber, which now contains only a very low content of H_2S , is passed via line 114 to an afterburner, not drawn, before the gas is discharged via a chimney, also not drawn.

EXAMPLE 1

An amount of sour gas of 9700 Nm³/h coming from a gas purification plant had the following composition at 45°C and 1.6 bar abs

60.0 Vol. %	H_2S
3.0 Vol. %	NH_3
30.0 Vol. %	CO_2
5.0 Vol. %	H_2O
2.0 Vol. %	CH_4

This sour gas was fed to a Claus plant with two Claus reactors. The sulfur formed in the sulfur recovery plant was, after the thermal stage and the catalytic reactor stages, condensed and discharged. The amount of sulfur was 7768 kg/h.

- 5 The sulfur recovery efficiency of the Claus plant, based on the sour gas, was 93.3%.

The amount of off-gas of 29749 Nm³/h coming from the Claus plant had the following composition at 164°C and a pressure of 1.14 bar abs.

10

	0.47	Vol. %	H ₂ S
	0.24	Vol. %	SO ₂
	0.03	Vol. %	COS
	0.04	Vol. %	CS ₂
15	0.01	Vol. %	S ₆
	0.04	Vol. %	S ₈
	1.38	Vol. %	CO
	1.53	Vol. %	H ₂
	11.37	Vol. %	CO ₂
20	55.96	Vol. %	N ₂
	0.66	Vol. %	Ar
	28.27	Vol. %	H ₂ O

- 25 This off-gas was supplied with 103 Nm³/h of hydrogen as reducing gas and then heated to 280°C to hydrogenate all sulfur dioxide (SO₂) and sulfur vapor (S₆, S₈) present to H₂S, and further to hydrolyze carbonyl sulfide (COS) and carbon sulfide (CS₂) to H₂S in the hydrogenation reactor which contains a sulfided group 6 and/or group 8 metal catalyst, in
30 this case a Co-Mo catalyst.

The amount of off-gas from the hydrogenation reactor was 31574 Nm³/h and had the following composition at 317°C and 1.10 bar abs.

35

	1.24	Vol. %	H ₂ S
	28	ppm	COS
	2	ppm	CS ₂
	2.02	Vol. %	H ₂
5	12.64	Vol. %	CO ₂
	56.62	Vol. %	N ₂
	0.67	Vol. %	Ar
	26.80	Vol. %	H ₂ O

10 The off-gas was then cooled to 72°C, a temperature which is 3°C above the dew point of the water vapor present in the off-gas.

 Then the cooled off-gas was treated in a bioplant at 72°C, with no water condensation from the off-gas taking
15 place. In the absorber of the bioplant, H₂S is washed from the off-gas with diluted sodium hydroxide solution, whereafter the solution with the absorbed H₂S was passed to an aerobic biological reactor in which the H₂S was converted to elemental sulfur.

20 In the bioplant no heat is supplied or removed, so that the absorption of H₂S and the conversion to elemental sulfur occurred at the same temperature of 72°C.

 To the aerobic reactor an amount of 945 Nm³/h of air was supplied for the selective oxidation of H₂S to sulfur. The
25 amount of gas from the absorber was 31189 Nm³/h and had the following composition at 72°C and 1.05 bar abs.

	250	ppm	H ₂ S
	28	ppm	COS
30	2	ppm	CS ₂
	2.04	Vol. %	H ₂
	12.80	Vol. %	CO ₂
	57.32	Vol. %	N ₂
	0.68	Vol. %	Ar
35	27.13	Vol. %	H ₂ O

Via an afterburning, this gas was passed to the chimney. The amount of sulfur formed in the biopant was 551 kg/h. The total amount of sulfur produced in the sulfur recovery plant and the biopant was 8319 kg/h, which raised the total
 5 desulfurization efficiency, based on the original sour gas, to 99.87%.

EXAMPLE 2

10 An amount of sour gas of 6481 Nm³/h coming from a gas purification plant had the following composition at 45°C and 1.6 bar abs

	90.0 Vol.%	H ₂ S
15	3.0 Vol.%	NH ₃
	5.0 Vol.%	H ₂ O
	2.0 Vol.%	CH ₄

This sour gas was supplied to a SUPERCLAUS® plant with
 20 two Claus reactors and a selective oxidation reactor. The sulfur formed in the sulfur recovery plant was, after the thermal stage and the catalytic reactor stages, condensed and discharged. The amount of sulfur was 8227 kg/h. The sulfur recovery efficiency of the Claus plant, based on the sour
 25 gas, was 98.5%.

The amount of off-gas of 21279 Nm³/h coming from the Claus plant had the following composition at 129°C and a pressure of 1.14 bar abs

30	0.03 Vol.%	H ₂ S
	0.20 Vol.%	SO ₂
	20 ppm	COS
	30 ppm	CS ₂
	10 ppm	S ₆
35	0.01 Vol.%	S ₈
	0.15 Vol.%	CO

	1.72	Vol.%	H ₂
	1.14	Vol.%	CO ₂
	62.45	Vol.%	N ₂
	0.74	Vol.%	Ar
5	33.05	Vol.%	H ₂ O
	0.50	Vol.%	O ₂

This off-gas was supplied with 133 Nm³/h of hydrogen as reducing gas and then heated to 280°C to hydrogenate all
10 sulfur dioxide (SO₂), sulfur vapor (S₈, S₆) present to H₂S and H₂O, and further to hydrolyze the carbonyl sulfide (COS) and carbon sulfide (CS₂) to H₂S in the hydrogenation reactor which contains a sulfided group 6 and/or group 8 metal catalyst, in this case a Co-Mo catalyst.

15 The amount of off-gas from the hydrogenation reactor was 22863 Nm³/h and had the following composition at 367°C and 1.10 bar abs.

	0.37	Vol.%	H ₂ S
20	2	ppm	COS
	0.82	Vol.%	H ₂
	1.90	Vol.%	CO ₂
	62.89	Vol.%	N ₂
	0.75	Vol.%	Ar
25	33.27	Vol.%	H ₂ O

The off-gas was then cooled to 76°C, a temperature which is 3°C above the dew point of the water vapor present in the off-gas.

30 Then the cooled off-gas was treated in a bioplant at 76°C, with no water condensation from the off-gas taking place. In the absorber of the bioplant, H₂S is washed from the off-gas with a diluted sodium hydroxide solution, whereafter the solution with the absorbed H₂S was passed to
35 an aerobic biological reactor in which the H₂S was converted to elemental sulfur.

In the bioplant, no heat is supplied or removed, so that the absorption of H_2S and the conversion to elemental sulfur occurred at the same temperature of $76^\circ C$. The aerobic reactor was supplied with an amount of $205 \text{ Nm}^3/\text{h}$ of air for the partial oxidation of H_2S to sulfur. The gas from the absorber was $22780 \text{ Nm}^3/\text{h}$ and had the following composition at $76^\circ C$ and 1.05 bar abs.

	75	ppm	H_2S
10	2	ppm	COS
	0.82	Vol. %	H_2
	1.91	Vol. %	CO_2
	63.12	Vol. %	N_2
	0.75	Vol. %	Ar
15	33.39	Vol. %	H_2O

Via an afterburning, this gas was passed to the chimney. The amount of sulfur formed in the bioplant was 119 kg/h . The total amount of sulfur produced in the sulfur recovery plant and the bioplant was 8346 kg/h , which raised the total desulfurization efficiency, based on the original sour gas, to 99.97%.

EXAMPLE 3

25

An amount of sour gas of $3500 \text{ Nm}^3/\text{h}$ coming from a gas purification plant had the following composition at $40^\circ C$ and 1.7 bar abs.

30	88.0	Vol. % H_2S
	6.1	Vol. % CO_2
	1.5	Vol. % CH_4
	4.4	Vol. % H_2O

35 This sour gas was supplied to a Claus plant with three Claus reactors.

The air supply to this Claus plant was set such that the reaction (2) in the thermal stage and in the Claus reactors was operated with excess H_2S , so that the $H_2S:SO_2$ content after the third reactor stage is greater than 100 to 1, so that the SO_2 content became less than 0.009 vol.%. 5

The sulfur formed in the sulfur recovery plant was, after the thermal stage and the catalytic reactor stages, condensed and discharged. The amount of sulfur was 4239 kg/h. The sulfur recovery efficiency of the Claus plant, based on 10 the sour gas, was 96.4%. The amount of off-gas of 10001 Nm^3/h coming from the Claus plant had the following composition at 130°C and a pressure of 1.15 bar abs.

	0.93	Vol.% H_2S
15	0.009	Vol.% SO_2
	0.04	Vol.% COS
	0.04	Vol.% CS_2
	0.001	Vol.% S_6
	0.01	Vol.% S_8
20	0.36	Vol.% CO
	1.83	Vol.% H_2
	2.79	Vol.% CO_2
	59.68	Vol.% N_2
	0.60	Vol.% Ar
25	33.71	Vol.% H_2O

The off-gas was then cooled to 78°C, a temperature which is 3°C above the dew point of the water vapor present in the off-gas. Then the cooled off-gas was treated in a bioplant at 30 73°C, with no water condensation from the off-gas taking place. In the absorber of the bioplant, H_2S is washed from the off-gas with diluted sodium hydroxide solution, whereafter the solution with the absorbed H_2S was passed to an aerobic biological reactor in which the H_2S was converted 35 to elemental sulfur. In the bioplant, no heat is supplied or

removed, so that the absorption of H_2S and conversion to elemental sulfur occurred at the same temperature of $73^\circ C$.

To the aerobic reactor an amount of $320 \text{ Nm}^3/\text{h}$ of air was supplied for the selective oxidation of H_2S to sulfur. The amount of gas from the absorber was $9901 \text{ Nm}^3/\text{h}$ and had the following composition at $73^\circ C$ and 1.05 bar abs.

	190	ppm H_2S
	7	ppm COS
10	9	ppm CS_2
	1.85	Vol.% H_2
	0.36	Vol.% CO
	2.82	Vol.% CO_2
	60.28	Vol.% N_2
15	0.61	Vol.% Ar
	34.06	Vol.% H_2O

Via an afterburning, this gas was passed to the chimney. The amount of sulfur formed in the bioplant was 156 kg/h . The total amount of sulfur produced in the sulfur recovery plant and the bioplant was 4395 kg/h , which raised the total desulfurization efficiency, based on the original sour gas, to 99.93%.

The small amount of SO_2 was converted to sulfate in the lye solution. In order not to obtain any build-up of sulfates, a small amount of 85 kg/h of the lye solution was discharged and replaced with a corresponding amount.

Claims

1. A method for removing H_2S from off-gases which contain at least 20% by volume of water vapor, comprising treating the off-gases at a temperature above the water dew point of the off-gases with an aqueous, alkaline solution under
5 absorption of the H_2S , followed by subjecting the sulfide-containing solution formed to a biological oxidation of the sulfide.
2. A method according to claim 1, wherein the absorption and oxidation occur at substantially the same temperature.
- 10 3. A method according to claim 1 or 2, wherein the off-gases to be treated come from a sulfur removal plant.
4. A method according to claim 3, wherein the off-gases are hydrogenated prior to the absorption.
5. A method according to claims 1-3, wherein the off-gases
15 have a molar H_2S/SO_2 ratio of at least 100 and preferably come from a Claus plant.
6. A method according to claims 1-5, wherein the off-gases contain 20 to 40% by volume of water vapor.
7. A method according to claims 1-6, wherein the sulfides
20 are converted in the aerobic biological oxidation to elemental sulfur.
8. A method according to claims 1-7, wherein the sulfur, after the biological oxidation, is separated from the liquid.
9. A method according to claim 8, wherein the liquid,
25 after separation of the sulfur, is recirculated as absorption liquid.