

COAL GASIFICATION: HIGH TEMPERATURE
H₂S REMOVAL IN A STEAM REGENERATIVE PROCESS
UNDER REALISTIC CONDITIONS.

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Abstract

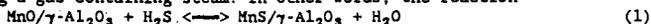
During gasification of coal H₂S, COS and some other impurities are formed. To remove H₂S and COS a steam regenerative process using MnO or FeO on γ -alumina acceptors has been developed. The acceptors can be used in the temperature range of 700-1100 K. Regeneration takes place at the same temperature with a gas containing steam. Using a 200 kW thermal coal gasification plant available at ECN in Petten the acceptors have been tested under realistic conditions at pilot plant scale. In this way the effects of other impurities and upscaling on acceptance and regeneration behaviour could be studied. No deactivation of the acceptors was found during four weeks of continuous sulfidation-regeneration cycles. Used/spent acceptors are analysed for capacity and contaminants.

Introduction

As the world oil and natural gas sources are limited quite some research effort is aimed at the utilisation of coal to replace oil and natural gas. The positive results of the demonstration plant in Cool Water, California, are now available. Also in the Netherlands the application of coal gasification for electricity production meets renewed interest which leads to a lot of new short and long term research proposals. The long term proposals mainly concern high temperature gas cleaning because this can lead to improvement of efficiency and lower investments in CGCC plants [1].

When coal is gasified it reacts with steam and air or oxygen at temperatures in the range of 800-2000 K. The raw gas produced by a gasifier generally contains a number of impurities, of which sulfur compounds are the major ones. Requirements of either downstream processes or environmental regulations usually dictate that these impurities must be removed from the gasifier effluent. The principle sulfur compound formed during gasification of coal is H₂S beside smaller amounts of COS, CS₂ and mercaptans. The total amount of H₂S produced can vary between 0.2-1.4 %v. After removing the sulfur compounds the gas can be used as a fuel, a synthesis gas or a reducing gas.

Both the gasification and the combustion of the purified gas are carried out at high temperatures. If purification is carried out at low temperature (e.g. in case ethanol amines are used) the raw gas must be cooled before entering the purification unit and reheated prior to combustion. However, if purification is also carried out at a high temperature the cooling and reheating can be eliminated or at least be simplified. The overall thermal efficiency of the whole plant will increase. Unfortunately, almost all commercially available processes for the removal of H₂S operate at low temperatures or can not be regenerated easily. Van der Linde [2] found that MnO on γ -Al₂O₃ can remove H₂S from gases at 700-850 K, while the sulfided product can be regenerated to MnO on γ -Al₂O₃ at the same temperature using a gas containing steam. In other words, the reaction



is reversible.

It has been shown by Soerawidjaja [3] that acceptors based on manganese or iron are superior to those based on cobalt, nickel and zinc. The active component in the reaction seems to be a surface spinel, MnAl₂O₄ or FeAl₂O₄. Using available thermodynamic data [4,5], equilibrium constants and enthalpy changes can be estimated. The thermodynamic equilibrium constants of the sulfidation of MnAl₂O₄ and FeAl₂O₄ in the temperature range of 700-1100 K become close to unity, while

those of MnO and FeO are large (greater than 100), see figure 1. This means that the sulfidation of $MnAl_2O_4$ and $FeAl_2O_4$ is reversible, whereas that of MnO and FeO is irreversible. From figure 2 it can be seen that the enthalpy changes accompanying sulfidation of these metal oxides, is small in case of $MnAl_2O_4$ and $FeAl_2O_4$.

Experimental.

Acceptor preparation.

Up till now the research has taken place in a laboratory set-up using approximately 3 g of grinded and sieved alumina extrudates with particle diameters between 0.25 and 0.42 mm while a synthetic gas mixture of N_2 , H_2 and H_2S was used. The experiments described here not only concern the use of a realistic gas but also involve upscaling: 1 kg acceptor per reactor. Also the particle diameter of the acceptor increased. The γ -alumina extrudates used (Ketjen/Akzo 001-1.5E) have an average length of 4.8 mm and an average diameter of 1.7 mm. Because of the increased particle diameter and the larger amount of carrier material the impregnation method had to be adjusted to maintain the metal content and sulfur removal capacity.

For acceptor preparation the scheme in figure 3 is followed. Normally the impregnation fluid is shaken a few times during impregnation (method 1), resulting in a good acceptor. However, this technique can not be used for larger amounts of acceptor material. The main problem with the large amount of material and coarse extrudates is contacting the impregnation fluid with the carrier material in such a way that each particle is filled with the impregnation fluid. A number of techniques to improve contacting between fluid and carrier are investigated: stirring fluid only (method 2), stirring of both fluid and solids (method 3) and recycling impregnation fluid through a packed bed of carrier material (method 4). Each acceptor batch prepared is analysed for attrition, distribution of the metal oxide in each particle and between particles, metal content and capacity for H_2S removal, the last property both under laboratory conditions and under realistic conditions.

The first two criteria are evaluated qualitatively only. The metal oxide distribution can, because the oxides are dark coloured, be evaluated easily. The metal content is determined by Atomic Adsorption Spectroscopy (AAS). The equipment used for determining breakthrough capacity under laboratory conditions is described elsewhere [6].

Equipment

The breakthrough capacity and deactivation under realistic conditions are measured in an experimental set-up situated at the Energy Research Foundation (ECN) in Petten, The Netherlands. The gasifier (200 kW thermal) is build especially for research purposes and produces a fuel gas that can be used for a number of different experiments; the unused gas is flared.

The pilot plant can be divided into two main parts: the coal gasifier which supplies the realistic fuel gas and the equipment for high temperature H_2S removal in which the acceptors can be tested.

The coal gasifier can be subdivided into: the reactor, the coal feed system, the air system and the hot fuel gas system

The co-current moving bed reactor consists of a steel vessel internally fully isolated with ceramic material. At the bottom an asymmetric ashcone rotates with a low variable speed and forces the ashes and unconverted coal into the ashes waste pipe.

The air needed for gasification is sucked into the reactor through two air inlets, one situated at the top and another in the middle of the reactor. This means that the gasifier is used at underpressure, preventing gas leakage to the environment.

The coal bed can be divided into three zones:

1. the pyrolysis zone at top of the coal bed. In this zone devolatilisation of the coal takes place. Light hydrocarbons and heavy tar products are formed. Particularly the heavy tar products can cause problems when they condensate. They are nearly completely converted in the oxidation zone.
2. the oxidation zone under the pyrolysis zone. In this zone tar and hydrocarbons are oxidized by the air which is led into the reactor just above the coal bed. Moreover, part of the coal is converted into CO_2 and H_2O to produce the heat needed by the reactions in the reduction zone. The temperature raises quickly to a level of 1600-1900 K.
3. the reduction zone at the bottom of the coal bed. In this zone the products of the oxidation zone, CO_2 and H_2O , react with coal to form CO and H_2 . Because these reactions are relatively slow the reduction zone covers the greatest part of the coal bed. The fuel gas exit is situated at the bottom of the reduction zone. In case browncoal is used as feed, as in the study presented here, the fuel gas leaves the reactor at about 1000 K.

The coal feed system consists of a storage bunker, a moving band to the top of the reactor and a lock hopper on top of the reactor.

The air system can be divided into the start-up system and the main system. At a cold start air is sucked through a separate pipe in which an electric heater is mounted. When the temperature of the coal has reached such a level that spontaneous combustion takes place and partial oxidation generates enough heat to support the gasification process the electric heater is switched off and the main supply system is used.

Dust and ashes are removed from the gas stream by two cyclones. From the cyclones the gas is led into a cooler where the temperature is lowered to approximately 315 K to protect the rootsblower which sucks the air through the reactor.

Part of the hot fuel gas (approximately 900 K) is drawn off before entering the cooler and sent to the equipment for H_2S removal.

In the equipment for H_2S removal (figure 4) the following parts can be distinguished: pretreatment of the fuel gas, reactor section, gas analysis, pretreatment of regeneration- and flush gas and process control, data acquisition and registration

The fuel gas leaves the gasifier with a temperature of about 900 K. As the gas cooles down during transport to the desulfurization unit it is reheated electrically to 880 K. The hot gas passes through a silicium carbide filter, in which the dust content decreases from about 1 g/Nm^3 to about 20 mg/Nm^3 , and flows to the reactor section.

The equipment is designed in such a way that H_2S can be removed continuously. Three reactors are required (R1..R3). During operation one reactor is in the acceptance stage, a second in the regeneration stage while the third reactor is flushed. After H_2S breakthrough of the reactor in the acceptance stage all reactors are switched to their next stage.

Each reactor is filled with 1 kg of acceptor material, MnO or FeO on a γ -alumina carrier. The temperature is kept at about 880 K by a heating jacket.

The raw fuel gas is sent downwards through the reactor. Regeneration and flushing take place in the opposite direction. In this way the removal of H_2S from the acceptors is faster and more complete (after acceptance most of the H_2S is accumulated in the top of the acceptorbed). For the regeneration a H_2O , H_2 , N_2 -mixture is used. Flushing is done with an H_2 , N_2 -mixture.

The H_2S concentrations in the raw fuel gas, the cleaned fuel gas and the regeneration off gas are needed to calculate mass balances and breakthrough capacities. Moreover, the CO_2 , CO and H_2O concentrations in the raw fuel gas are measured.

Three different analysis apparatuses are used: a Beckman gas chromatograph, a Radas H_2S -monitor and a Metrohm titration unit. The H_2O concentration in the raw fuel gas is measured from time to time separately. The gas chromatograph measures the composition of the raw fuel gas. The monitor registers the H_2S concentration in the

cleaned fuel gas by means of UV absorption. Two ranges can be chosen: 0-500 and 0-5000 ppm. The titration unit is used to measure the amount of H_2S produced during regeneration. For this purpose a pump continuously sucks a flow through a critical capillary from the regeneration off-gas into a titration vessel. By using different capillaries the flow can be changed (50, 100 or 150 Nml/min). The titration unit is the same as described with the laboratory set-up [5].

The mini plant is automated by a system which consists of a Tulip AT personal computer, equipped with a Keithley 570 interface and runs under the software package Asyst.

The system has the following tasks:

- control of the acceptance-regeneration cycles in the three reactors, using 12 channels. A number of boundary conditions, e.g. time elapse of the stages, measurement of breakthrough and safety, are taken into account.
- data acquisition of three different channels and filing of the data gathered in a clear structure.
- presentation of the data in such a way that mass balances can be calculated and the course of the breakthrough capacity as a function of time (days) can be followed.

The plant can be used 24 hours a day. Each acceptance-regeneration cycle results in three sets of data: the H_2S concentration in the raw- and in the cleaned fuel gas (gas chromatograph and monitor respectively) and, from the regeneration stage, the amount of H_2S in the regeneration off-gas (from the titration unit).

Results and discussion

Table 1 shows the necessity of improving contact between impregnation fluid and carrier material. Shaking of the fluid from time to time (method 1) results in a poor distribution of the metal oxide, a low metal content and a low capacity (batch 1). Stirring the fluid only (method 2) gives attrition. This attrition could be lowered by stirring at a lower speed, but applied to larger quantities the contact is influenced negatively. The results of batch 3 show that stirring of both fluid and solids (method 3) results in too large attrition as well. The results of batch 4 show, in contrast with methods 1, 2 and 3, that method 4 (recycling the impregnation fluid through a packed bed of carrier material) improves contact between carrier and impregnation fluid. Attrition, distribution of the metal, metal content and capacity correspond with previous work [3]. Batches 5 to 9 confirm these observations.

The breakthrough capacities obtained in the laboratory set-up are generally somewhat lower than the optimum capacity (0.70-0.85 with regard to 0.80-1.0 $X_w S$). The use of larger particles is the main reason.

Decreasing impregnation time from about 18 hours to 2 to 3 hours has no influence on breakthrough capacity.

The results of the iron containing batches 10 and 11 are similar to those of previous work [3] if attrition, distribution of the metal, metal content and breakthrough capacity are taken into account.

Batches 10, 6 and 9 were tested continuously during four weeks under realistic conditions in reactors 1, 2 and 3 respectively. Each reactor was submitted to about 50 acceptance-regeneration cycles. The measurements which are most reliable with respect to their mass balance are discussed below. Examples of the acceptance and regeneration curves are shown in figures 5 and 6.

In figures 7, 8 and 9 the breakthrough capacities, the amount of H_2S released during regeneration and the CO and H_2O concentrations are presented as a function of cycle number. Most of the H_2O concentrations in the figures were not measured quantitatively but result from equilibrium calculations, in which it is supposed that thermodynamic equilibrium between CO, CO_2 , H_2 and H_2O is reached at the desulfurization reactor inlet. As the measured points (the dots in the figures) lie somewhat higher than the calculated points, the calculated points only give an indication of the course of the water concentration.

It can be noticed easily that the acceptance- and regeneration capacities follow the CO concentration line. Increasing the CO concentration increases the

breakthrough capacity. This effect was expected because the shift reaction will consume H_2O formed during acceptance and H_2O from the feed gas according to:



From the figures it can also be concluded that the breakthrough capacity remains almost constant. In tables 2 and 3 the average breakthrough capacity and the average composition of the raw fuel gas are given.

If the breakthrough capacities obtained under realistic conditions are compared with those obtained in the laboratory set-up with a gas containing 20 %v CO, 10 %v H_2 , 5 %v H_2O and 1 %v H_2S there is a reasonable agreement. The breakthrough capacity is about 0.40 %w S for a manganese containing acceptor. The influence of the CO_2 and the higher H_2 concentration (both causing a somewhat lower capacity) is not corrected for.

When the desulfurization process described here would be applied to the Shell coal gasification process the breakthrough capacity would be much higher. As the raw fuel gas contains about 65 %v CO, 26 %v H_2 and 2 %v H_2O [7], a breakthrough capacity of approximately 1.5 %w S can be expected.

The H_2S concentration in the cleaned fuel gas depends upon gas composition, e.g. H_2O - and CO concentration. Before breakthrough the concentration in the cleaned fuel gas is lower than 40 ppmv and generally lower than 20 ppmv. Purification to a level below 1 ppmv is measured frequently.

Recently testing of new batches of the acceptors has started. At this moment batches 7, 11 and 8 (reactors 1, 2 and 3 respectively) are used during two weeks. The breakthrough capacities and regeneration behaviour are better than the results of batches 10, 6 and 9, see figure 10. From the figures it can be concluded that the acceptors show the same initial deactivation as observed during experiments in the laboratory. After this initial period the breakthrough capacity remains almost constant. Because the acceptors are still being used, they are not tested under laboratory conditions yet. Results will be available in the first half of 1990.

The H_2S concentration in the dried regeneration off gas is about 15 %v, high enough to be delivered to a Claus plant. This concentration can be increased by optimizing the composition of the regeneration gas. Under laboratory conditions, concentrations up to 40 %v (on a dry base) have been measured [8].

After the experiments at EGN the used/spent acceptors were tested again under laboratory conditions. The breakthrough capacities showed to be lower than expected, probably due to sintering of the carrier material. This sintering can be caused by undesirable high temperatures (up to 1000 K) as were measured in the reactors. In table 4 the results are summarized. The breakthrough capacities of the fresh and used/spent acceptors are obtained under exactly the same conditions. The breakthrough capacity of the manganese based acceptors decreased stronger than that of the iron based acceptor. This difference could be explained by the fact that the iron based acceptor is not used for testing the equipment. Some samples of the used/spent acceptors were analysed with XPS (X-ray Photoelectron Spectroscopy) and ESCA (Electron Spectroscopy for Chemical Analysis) to determine surface composition of the acceptors. Clearly some carbon, sulfur, nitrogen and chloride is present and, of course, aluminium and manganese or iron.

Conclusions

From the experiments it can be concluded that:

- the experimental set-up for testing acceptors under realistic conditions including process control and data acquisition operates without any serious problems.
- during the test period no deactivation of the acceptors is observed.
- during the second test period the acceptors have a higher capacity.
- the fuel-gas is cleaned to a level of 0-20 ppmv.
- the breakthrough capacity of the acceptors is quite low, a feasibility study has to indicate whether this is a main problem.

- the iron based acceptor seems to be less sensitive to deactivation caused by the use of a realistic fuel gas than the manganese based acceptors, but this difference could be explained by testing the equipment with the manganese containing acceptors.
- the H₂S concentration in the regeneration off-gas is high enough to deliver to a Claus plant, and can be optimized further.

Literature

1. J.J.M. Snepvangers, J. Stork, Kolanvergassing anno 1987, NEOM Publication, 874703/2319, August 1987.
2. B.J. van der Linde, An experimental study on the use of manganese oxide on γ -alumina acceptors for the flue gas desulfurization, Thesis, Delft University Press, 1982.
3. T.H. Soerawidjaja, Steam regenerative H₂S removal at high temperatures using metal oxide on alumina acceptors, Thesis, Delft University Press, 1985.
4. J. Barin, O. Knacke, O. Kubachewski, Thermochemical Properties of Inorganic Substances, Springer Verlag, Berlin, 1973, Supplement 1976.
5. D.R. Stull, H. Prophet, JANAF Thermodynamical Tables, 2nd ed., National Bureau of Standards, Washington D.C., 1971.
6. J.P. Wakker, A.W. Gerritsen, High Temperature H₂S Removal from Process Gases in a Steam Regenerative Process Using MnO or FeO on γ -alumina Acceptors, presented at this meeting.
7. L. David Smith (ed.), Deer Park unit points the way, Modern Power Systems, 3(8), August 1988.
8. R. van der Heijden, A.W. Gerritsen, Regeneratieve verwijdering van zwavelwaterstof bij 600°C, I²-Procesttechnologie, 10, 11-18, 1987.

Table 1. Results of acceptor preparation and characterization.

Batch #	Metal	Preparation				Results				
		Alumina (kg)	Volume (l)	Impregnation		Attrition	Metal distribution		Metal content (Zwt)	Capacity (Zwt S)
				Method	Time (h)		Per particle	Between particles		
1	Mn	0.02	0.07	1	18	no	bad	bad	6.10	0.50
2	Mn	0.02	0.07	2	18	yes	good	bad	5.03	0.45
3	Mn	0.02	0.07	3	18	yes	good	bad	5.17	0.55
4	Mn	0.45	1.50	4	18	no	good	good	8.26	0.80
5	Mn	1.08	3.54	4	18	no	good	good	8.44	0.70
6	Mn	1.80	5.94	4	18	no	good	good	7.51	0.80
7	Mn	1.80	6.00	4	24	no	good	good	8.46	0.70
8	Mn	2.00	6.00	4	3	no	good	good	8.09	0.85
9	Mn	1.90	6.30	4	2	no	good	good	8.98	0.70
10	Fe	1.90	6.30	4	18	no	good	good	6.95	0.55
11	Fe	1.50	5.00	4	3	no	good	good	5.17	0.55

Table 2. Average breakthrough capacities of acceptors under realistic conditions.

Acceptor	Breakthrough capacity (Zw S)
FeO (reactor 1)	0.25
MnO (reactor 2)	0.20
MnO (reactor 3)	0.18

Table 3. Average fuel gas composition.

Compound	Zv
CO	16.6
H ₂	17.0
CO ₂	12.6
H ₂ O	3.8 (from eq. calc.)
H ₂ S	0.3-0.4
CH ₄	0.9
dust	20 mg/Nm ³

Table 4. Breakthrough capacities of fresh and used/spent acceptors.

	Batch	Acceptor	Capacity fresh (Zw S)	Capacity used/spent (Zw S)	Deactivation (%)
Reactor 1	10	FeO	0.55	0.35	36
Reactor 2	6	MnO	0.80	0.39	51
Reactor 3	9	MnO	0.70	0.35	50

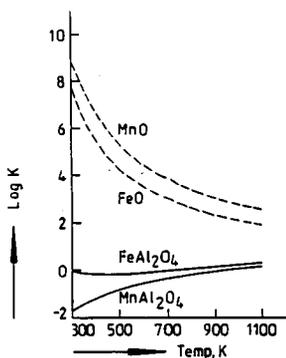


Figure 1. Thermodynamic data of sulfidation, equilibrium constants.

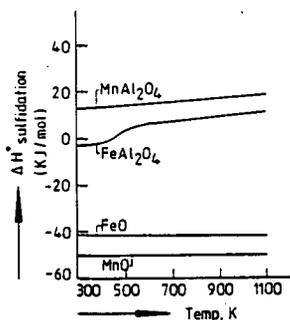


Figure 2. Thermodynamic data of sulfidation, heat of reaction.

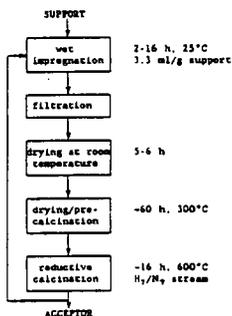


Figure 3. Preparation of acceptors.

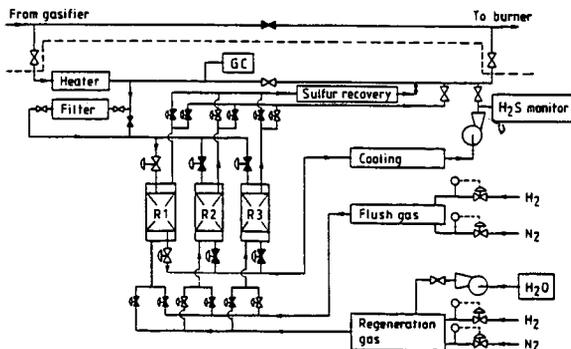


Figure 4. Schematic flow sheet of the pilot plant for H₂S removal.

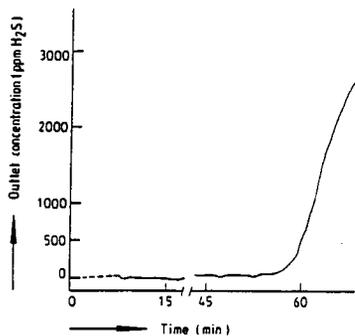


Figure 5. Measured breakthrough curve.

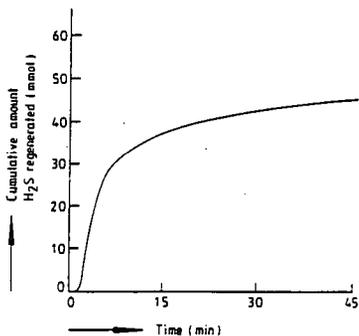


Figure 6. Measured regeneration curve.

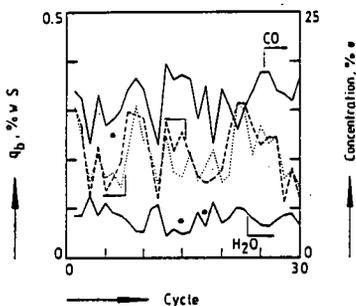


Figure 7. Captured and regenerated amount of sulfur of reactor 1. $\text{FeO}/\gamma\text{-Al}_2\text{O}_3$, batch 10 and the CO and H_2O concentrations.
 - - - Captured amount sulfur
 ····· Regenerated amount sulfur
 ● Measured H_2O concentration

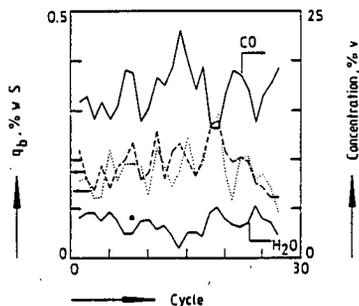


Figure 8. Captured and regenerated amount of sulfur of reactor 2. $\text{MnO}/\gamma\text{-Al}_2\text{O}_3$, batch 6 and the CO and H_2O concentrations.
 - - - Captured amount sulfur
 ····· Regenerated amount sulfur
 ● Measured H_2O concentration

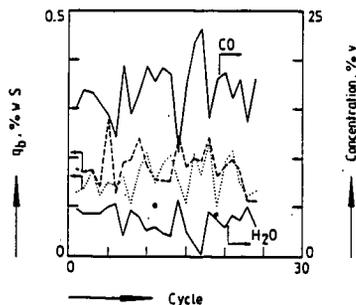


Figure 9. Captured and regenerated amount of sulfur of reactor 3. $\text{MnO}/\gamma\text{-Al}_2\text{O}_3$, batch 9 and the CO and H_2O concentrations.
 - - - Captured amount sulfur
 ····· Regenerated amount sulfur
 ● Measured H_2O concentration

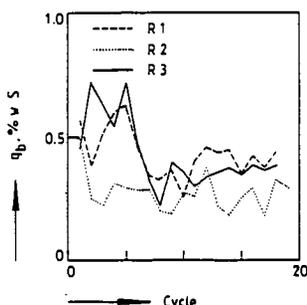


Figure 10. Breakthrough capacities of bacnes 7 (---), 11 (····) and 8 (—).