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A high capacity manganese-based sorbent for regenerative high temperature desulfurization with direct sulfur production
Conceptual process application to coal gas cleaning

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Abstract

A high capacity, monolith or particle shaped, regenerable sorbent has been developed for the desulfurization of a dry type coal gas. It consists of crystalline $MnAl_2O_4$, a small amount of disperse MnO, and an amorphous Mn–Al–O phase. Elemental sulfur is the only observed regeneration product during regeneration with SO_2. The sorbent can be used in the temperature range between 673 and 1273 K but the optimum capacity is utilized between 1100 and 1200 K. For regeneration with SO_2 the regeneration temperature should be >873 K to avoid sulfate formation. The sulfur uptake capacity is high and amounts up to 20 wt.% S and the sorbent performance appears to be stable during at least 110 sulfiding and regeneration cycles at 1123 K. For temperatures above 1100 K thermodynamic calculations are in accordance with the observed (solid) phases after sulfiding and regeneration, indicating the predictive potential for high temperatures. The performance of the surface sites that play an important role during desulfurization can, however, not be predicted. The regenerative removal of H_2S, COS, HCl and HF can possibly take place simultaneously with the same sorbent.

A new conceptual process configuration for high temperature coal gas cleaning and sorbent regeneration is proposed. Compared to other processes, less heat exchange equipment is required and no Claus unit is necessary to convert the regeneration product to sulfur.

Keywords: Absorption; Fuel; Gases; Processing; Sulfur; Manganese aluminate

1. Introduction

About one-third of the world's energy fuel consumption is in generating electricity of which almost 60% is produced from fossil fuels. Despite the relatively large emission of CO_2 during coal combustion and conversion the role of coal in electricity production and the production of chemicals is expected to become more important. An efficient way to convert coal to electricity is via a gasification process. Gasification of coal uses 20–30% of the oxygen theoretically required for complete combustion to carbon dioxide and water.

The composition of the coal gas is variable and dependent on the type of coal, feed system, gasifier, the oxidant and the gasification temperature. Carbon monoxide and hydrogen are the principal products, in particular at high temperature.

Coal gas contains several impurities, in particular dust and H_2S are the most important ones. In addition, usually significant amount of alkali metals, heavy metals, HCl, HF and NH_3 are present. Gas cleaning is not only necessary to prevent pollution of the environment, but also to protect the equipment against corrosion. For the currently used low temperature cleaning processes the gas is cooled with a large syngas cooler from about 1750 K to about room temperature. The impurities are removed in several washing steps with liquid sorbents. During regeneration of these sorbents, in most cases, H_2S sets free and is converted in a Claus plant to elemental sulfur. High temperature gas cleaning is attractive as it enhances the process efficiency. Direct sulfur production during regeneration is attractive as the expensive Claus plant becomes redundant.

The optimal temperature for hot gas cleaning is subject to debate. It appears that the benefit of hot gas cleaning compared to low temperature scrubbing is most clearly present up to say 575–675 K. The reason is that phase transitions are omitted. Materials that can withstand high temperatures are more costly. As a consequence, 675 K is often considered as the optimal cleaning temperature. On the other hand, a dedicated hot gas cleaning process operating at temperatures

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above 675 K might lead to additional large savings because heat exchange equipment is omitted. A good example is the radiation gas cooler present in high temperature gasifiers—gas turbine setups [16]. Moreover, other new technologies emerge, such as the solid oxide fuel cell (SOFC), which might operate with fuel gas at much higher temperatures. This work is focused on application of new high temperature technology.

The incentive of this research is to develop a regenerable sorbent to remove impurities from coal gas between 1000 and 1200 K. We restrict ourselves to the cleaning of a dry (0.4–2 mol% H_2O) coal gas and aim direct sulfur production during regeneration to avoid the expensive Claus process. It is anticipated that the sorbent can also be applied to other applications, for example, the desulfurization of fuel gas obtained from the gasification of heavy residues from oil industry.

1.1. Sorbent selection

The most important factors to be considered in process design and sorbent selection are schematically given in Fig. 1.

In the sorbent selection usually the uptake step is emphasized. However, the regeneration step is even more critical.

The first point in selecting a regeneration step is the decision about the desired product: should it be S, SO_2, or H_2S. In general, most favorable is the production of elemental S, followed by H_2S and SO_2.

At present, regeneration with oxygen is most common, giving SO_2 [1,2,9,15,18]. The reaction with oxygen is, however, very exothermic. To avoid local overheating the oxygen or air has to be diluted, resulting in very diluted SO_2 as a product of the regeneration. This is not favorable in view of the subsequent reaction into elemental sulfur in a Claus unit. For some sorbents regeneration is possible with H_2O leading to the formation of H_2S. However, a good regenerability with H_2O also means a high sensitivity for H_2O during the uptake step. For the direct production of elemental sulfur regeneration with SO_2 is an option. In that case regeneration and Claus reaction are coupled in one reactor. Sulfate formation is, however, in many cases is a problem [10,12,19].

1.1.1. Thermodynamics

The thermodynamics of sulfidation and regeneration reactions of manganese oxides and manganese aluminate ($MnAl_2O_4$) with different reactants, viz. O_2, H_2O, SO_2, CO_2, and H_2 have been evaluated. Furthermore, possible reactions with other components, such as HCl, HF, CO, H_2, HCN and NH_3, present in coal gas are dealt with.

The equilibrium compositions have been calculated by minimizing the Gibbs energy, using the program “Chemsage 3.0” with “Microterm” database. It should be noted that such a program calculates the thermodynamics of the bulk material and it is assumed that the solid phase has a constant “activity”. Below this is discussed further.

When the solid phase is in excess one can assume that the activity of the solid is constant and, as a consequence, the equilibrium K_{eq}^{b} constant can be expressed as the ratio of the gas phase concentrations. So for the sulfiding of a metal oxide:

$$\mathrm{MeO\,(bulk)} + H_2S \rightleftharpoons \mathrm{MeS\,(bulk)} + H_2O \qquad (1)$$

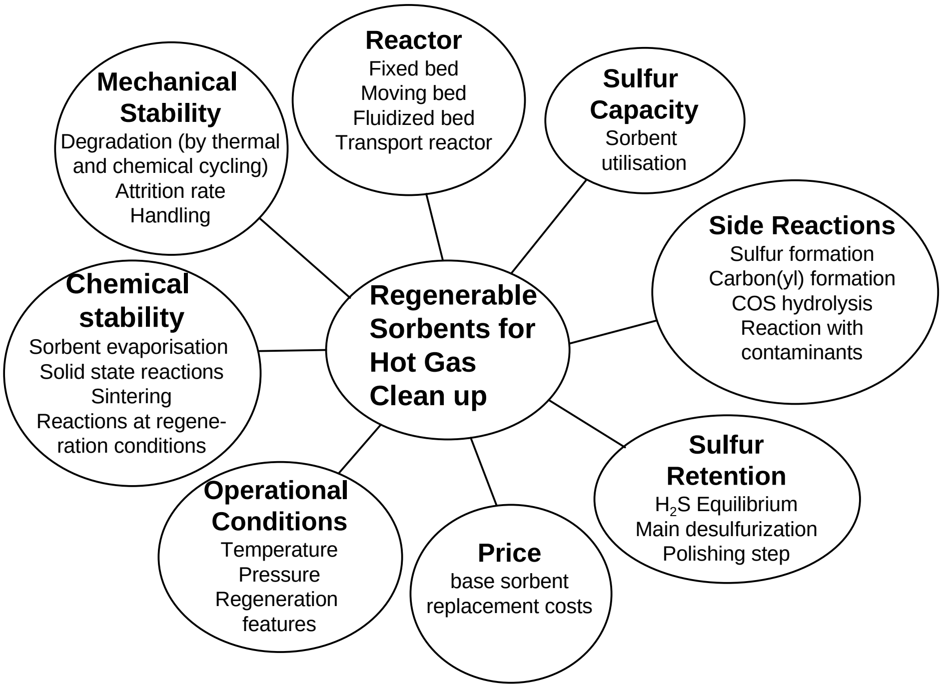

Fig. 1. Important factors for regenerative high temperature desulfurization with solid sorbents [8].

$$K_{\mathrm{eq}}^{\mathrm{b}} = \left\{ \frac{[\mathrm{H_2O}]}{[\mathrm{H_2S}]} \right\}_{\mathrm{eq}} \qquad (2)$$

These two equations show that if the $[H_2O]/[H_2S]$ ratio is larger than $K_{\mathrm{eq}}^{\mathrm{b}}$, the sulfided phase is unstable and will disappear, and if the ratio is higher than $K_{\mathrm{eq}}^{\mathrm{b}}$, H_2S uptake takes place and a sulfided phase is formed.

In a previous work [14,17] it was assumed that mainly surface sites act as acceptor sites during the sulfidation. In analogy to heterogeneous catalysis one can argue that surface site concentrations are not constant. When this separate surface phase consisting of sulfidable sites is taken into account they should also be included in the equilibrium expression:

$$\mathrm{MeO\,(surface)} + \mathrm{H_2S} \rightleftharpoons \mathrm{MeS\,(surface)} + \mathrm{H_2O} \qquad (3)$$

In a thermodynamic sense the surface is considered to be a separate phase. The equilibrium constant $K_{\mathrm{eq}}^{\mathrm{s}}$ can be defined as

$$K_{\mathrm{eq}}^{\mathrm{s}} = \left\{ \frac{[\mathrm{H_2O}]}{[\mathrm{H_2S}]} \frac{[\mathrm{MeS\,(surface)}]}{[\mathrm{MeO\,(surface)}]} \right\}_{\mathrm{eq}} \qquad (4)$$

To obtain good desulfurization, thermodynamics requires that either, $K_{\mathrm{eq}}^{\mathrm{b}}$ should be sufficiently high (Eq. (2)) or the sorbent should have a high surface area (Eq. (4)), resulting in a good surface capacity, even if bulk sulfide would be non-existing according to thermodynamics.

A contribution of surface sites to the desulfurization and regeneration performance has only been reported for manganese-based sorbents [3–8,14,17].

Regeneration with SO_2 can be expressed as

$$\mathrm{MeS} + 0.5\mathrm{SO_2} \rightleftharpoons \mathrm{MeO} + 0.75\mathrm{S_2} \qquad (5)$$

Figs. 2–6 show the most important results of the calculations. For more details the reader is referred to [7,8]. Both manganese oxides and manganese aluminate absorb H_2S over the temperature range studied. Compared with $MnAl_2O_4$, manganese oxides absorb H_2S and COS more strongly. Consequently, regeneration of sulfided manganese oxides is relatively difficult and oxygen is needed for regeneration. Sulfided $MnAl_2O_4$ can be regenerated with either SO_2 or H_2O leading to elemental sulfur (above 900 K, Eq. (5)) or H_2S (Eq. (1)), respectively. It is concluded that desulfurization of dry coal gas with $MnAl_2O_4$ is attractive because elemental sulfur can be produced during regeneration. If water is present the presence of some MnO is favorable because MnO absorbs H_2S better than $MnAl_2O_4$ in the presence of water (Fig. 2).

HCl and HF are also absorbed by MnO and $MnAl_2O_4$ (Fig. 3). At high temperatures H_2S and COS absorb preferentially. An advantage from a process point of view is that $MnCl_2$ on Al_2O_3, in principle, does not react with SO_2 but relatively easy with steam. This might enable a component specific regeneration.

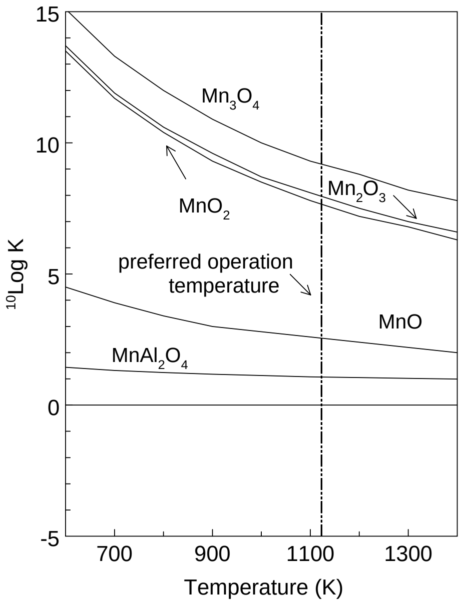

Fig. 2. Equilibrium constants of different manganese oxides and $MnAl_2O_4$ for reaction with H_2S (Eqs. (2), (6) and (7)).

Application of SO_2 for the regeneration is for most metal oxides associated with undesirable sulfate formation. For MnS on alumina, however, above 700 K direct regeneration with SO_2 is possible without sulfate formation. This is clearly shown in Fig. 6. Besides the formation of sulfur (as S_2) it is predicted that a small amount of S_2O is also formed.

In general it is, of course, not possible to decide on the best adsorbent independently of the specific application.

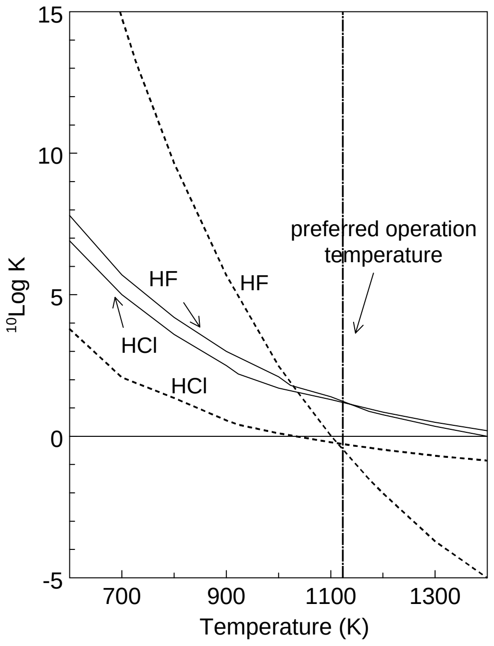

Fig. 3. Equilibrium constants for reaction of MnO (solid lines) and $MnAl_2O_4$ (dashed lines) with HF and HCl.

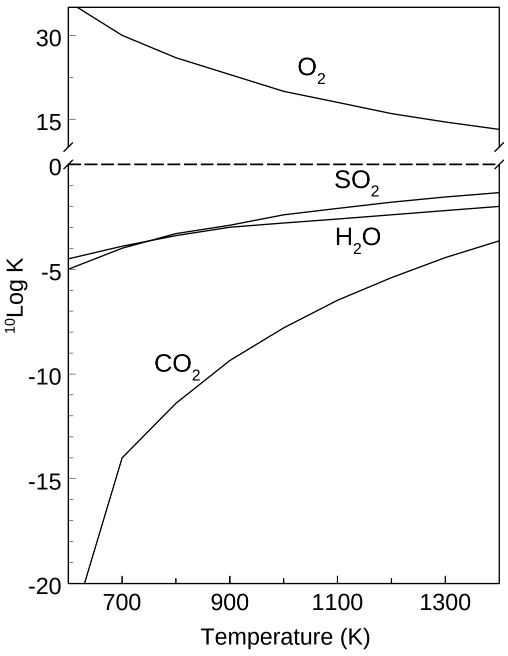

Fig. 4. Thermodynamic equilibrium constants of the reaction of MnS to MnO with different regenerants (Eq. (8)).

In the present study, Mn-based sorbents have been chosen because it is felt that:

- they have sufficient desulfurization potential for dry coal gas at high temperatures (873–1173 K) and can also remove HF and HCl;
- direct production of elemental sulfur during regeneration is thermodynamically feasible without sulfate formation;
- they are robust and stable and because Mn oxides and sulfides are not reduced to the elemental metal and its metal chlorides, fluorides are not very volatile compared to many other metals. Moreover, carbonyl compounds are eliminated by manganese sorbents and coke formation is expected not to occur.

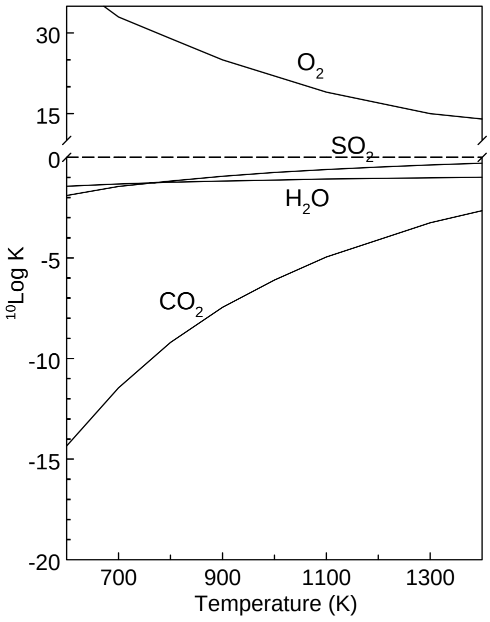

Fig. 5. Thermodynamic equilibrium constant of MnS/Al_2O_3 to $MnAl_2O_4$ with different regenerants (Eq. (9)).

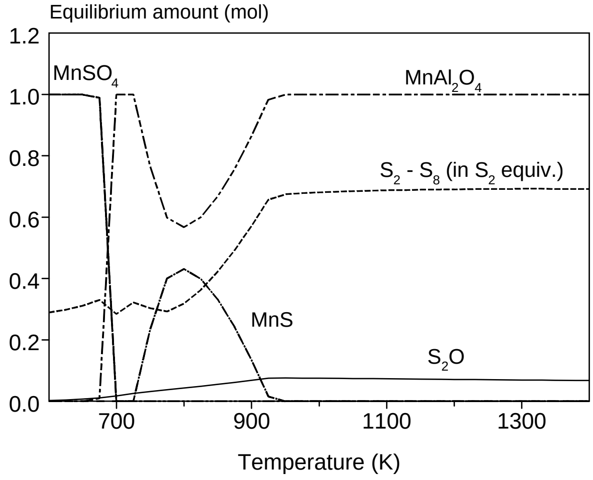

Fig. 6. Thermodynamic equilibrium composition for regeneration of 1 mol MnS on Al_2O_3 with 10 mol SO_2.

2. Experimental

2.1. Acceptor materials

The acceptor material was prepared by wet impregnation of the carrier material. Three types of acceptor material were used: pure γ-Al_2O_3 monoliths (M), cordierite monoliths with about 25 wt.% γ-Al_2O_3 washcoat layer (MW), and particles (P) in different size fractions ranging from 60 to 400 μm. The largest particles were made by crushing and sieving of extrudates. The monoliths of 10 mm in diameter had a cell density of 62 cells/cm^2 (400 cpsi).

Monolith supports were included in the research because compared to particles, if applied in a fixed bed, their insensitivity to dust, low pressure drop over the bed, and relatively short diffusion path are very attractive features [3,4].

2.1.1. Wet impregnation

The carrier material was contacted with a 1.5–2 mol/l aqueous solution of $MnAc_2{\cdot}4H_2O$, which was continuously circulated through the monolith channels or around the particles during impregnation. The impregnation time varied was typically 8 h and the temperature around 310 K. After impregnation the excess solution was removed from the channels with pressurized air (monoliths) or by centrifugation (particles). The samples were dried in a microwave oven (115–230 W). The drying time was dependent on the sample weight and was 3–6 min for 25 g sample. After drying in the microwave the samples were kept for 12 h in a conventional oven at 353 K. Calcination was performed in static air at 873–973 K for at least 6 h. The γ-Al_2O_3 monoliths/particles and the wash coated monoliths had about a 6–8 and 3 wt.% manganese loading, respectively, after a single impregnation with a 2 mol/l solution. To obtain higher manganese loadings (up to 40 wt.% Mn) the procedure was repeated. The samples are indicated by their type (M, MW or P) and Mn content in wt.%.

2.1.2. Characterization of the acceptors after sulfiding and regeneration

After sulfiding and regeneration the acceptors were characterized with a number of techniques: XRD, BET, pore volume, TEM, AAS and EDX. These analysis were performed to correlate (a change in) the composition and morphology of the sorbent, to the sulfiding and regeneration performance at specific operation conditions. Only the XRD results are shown in this article. The results of other techniques will be discussed briefly. For more details the reader is referred to [8].

2.2. Absorption and regeneration experiments

Absorption and regeneration tests were carried out using monoliths and particles with different manganese loadings. In this article we focus on the samples with a Mn loading between 32 and 40 wt.% Mn. The most important points of investigation during these tests are sulfur uptake capacity, desulfurization depth, operation temperature, and regeneration with SO_2 and H_2O, and stability of the sorbent.

The experimental setup was equipped with a gas dosing section, a sulfiding and regeneration section, and an analysis section. The analysis section contained an UV-Vis spectrophotometer (Cary-1, Varian, 230 nm used for H_2S detection), a thermal conductivity detector (TCD, VICI) and a quadrupole mass spectrometer (MS; Leybold/Inficon). Water and H_2S were removed after passing the UV spectrophotometer with a tubular membrane dryer of Nafion® (Perma Pure) and zinc oxide bed at 723 K, respectively. In case the MS was used the zinc oxide bed and the TCD were bypassed. Gases were supplied with thermal mass flow controllers and led to a quartz reactor tube. The inner diameter of this tube was 6 mm for particles and 10 mm for monolith samples. The bed length was typically a few centimeters and the sample weight typically between 0.25 and 1 g. If desired, water was added to the regeneration or sulfiding gas by passing argon through a saturator.

In general, the experiments involved a number of cycles. Most cycles consisted of four steps: sulfiding, flushing, regeneration, and flushing. Before and after every step the composition of the feed gas, and during a step the composition of the gas leaving the reactor was measured. For standard sulfiding experiments the feed gas contained 50 mol% H_2, 1 mol% H_2S and 49 mol% argon. The total pressure and flowrate were 0.14 MPa and 56 μmol/s, respectively. For the simulated coal gas experiments the feed contained 17 mol% H_2, 35 mol% CO, 0.64 mol% H_2S and 2.1 mol% H_2O.

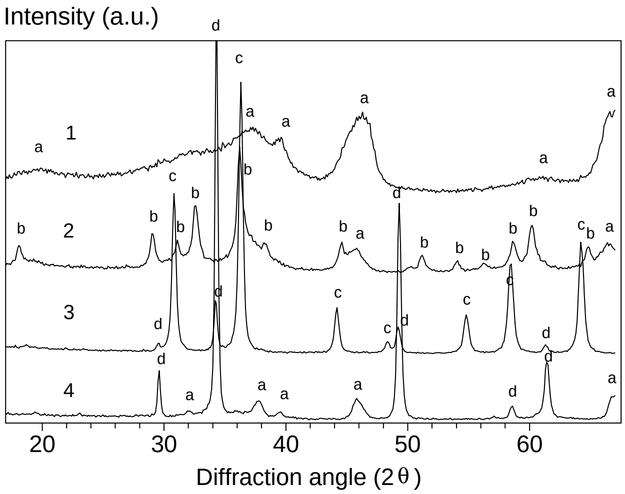

Fig. 7. XRD patterns for a fresh unloaded γ-Al_2O_3 monolith (1, M0), fresh impregnated and calcined (at 973 K) monolith (2), a regenerated monolith (3), and a sulfided monolith (4): (a) γ-Al_2O_3; (b) Mn_3O_4; (c) $MnAl_2O_4$; (d) MnS (2, 3, and 4 are M32 samples).

For standard regeneration experiments with SO_2 and water 50 and 30 mol% have been used, respectively. Argon was used as balance.

Fig. 8 shows a typical profile of the UV signal at 230 nm during one cycle with steam regeneration at 1123 K. This signal is proportional to H_2S concentration. Steam regeneration is taken as an example here because of the ease of transient H_2S detection compared to transient S_2 detection. Elemental sulfur was condensed after the reactor and weighed.

3. Results

3.1. Characterization

Fig. 7 shows XRD patterns of a fresh unloaded γ-Al_2O_3 monolith, a fresh impregnated and calcined monolith, a steam regenerated monolith, and a sulfided monolith. The XRD of the fresh unloaded sample shows the diffraction pattern of γ-Al_2O_3 (10-425; International Center for Powder Diffraction Data, 1992). The XRD of the fresh impregnated and calcined monolith shows the diffraction patterns of Mn_3O_4 (16-154) only superimposed on the pattern of γ-Al_2O_3. The XRD of the (sulfided and) regenerated[1] sample shows mainly $MnAl_2O_4$ (29-880), but also some MnS (6-518). The XRD of the sample which is sulfided[2] shows MnS (6-518) and γ-Al_2O_3. The particle size of the manganese species in pattern 2-4 is estimated with the Scherrer formula (Guinier, 1963) to be in between 10 and 20 nm.

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[1] After two sulfiding/regeneration cycles at 1123 K.

[2] After three sulfidings and two regenerations at 1123 K.

Table 1
BET surface area of different samples before and after use at 1123 K

Sample code	wt.% Mn (g_{Mn}/g_{active})	History	Regenerant	S_{bet} (m^2/g_{active})
MW36	36	Fresh		76
		After 75 cycles	Steam	14
P36	36	Fresh		80
		After 53 cycles	SO_2	13
		After 50 cycles	$SO_2 + SO_2/O_2$	6

Regeneration with SO_2 at 1123 K resulted in comparable XRD profiles (not shown) as depicted in Fig. 7. However, after regeneration with SO_2 below 873 K, XRD also reveals sulfate, and after regeneration at 1123 K with oxygen or SO_2/O_2 XRD shows some MnO.

TEM revealed that regenerated and sulfided samples contained a considerable amount of amorphous phases besides crystalline phases also. TEM/EDX showed the presence of very small MnO rich particles in regenerated samples and MnS particles in sulfided samples.

In Table 1 the surface area for several samples is given; fresh, after impregnation and calcination, and after a number of cycles. For most impregnated samples which are regenerated with steam or SO_2 the same behavior is observed: a strong decrease of the surface area in the first cycle, and stabilization around 14 m^2/g. In general, sintering is more severe for samples which were regenerated with a SO_2/O_2 mixture.

3.2. *Isothermal cycles*

3.2.1. *Desulfurization depth*

Typical curves for sulfiding with a dry feed and regeneration with steam at 1123 K are presented in Fig. 8. During sulfiding the sample initially adsorbs all H_2S and essentially no H_2S is detected at the exit of the reactor. (The detection limit was about 5 ppm.) After a certain time, breakthrough occurs and the signal stabilizes at the feed level.

In general, the outlet concentration of H_2S during sulfiding is between 5 and 50 ppm depending on the H_2S, CO, H_2O and H_2 concentrations, and the temperature. Tests with simulated coal gas showed similar results [7,8]. No coke formation was observed.

If the water content present in the feed is above 2.5% two breakthrough levels are observed after a period of complete absorption. The first one is relatively low and constant; the second level is much higher followed by a slow approach towards the feed concentration. The observed $[H_2O]/[H_2S]$ (Eq. (2)) exit level ratios for these regions are 220 and 10, respectively, at 1123 K with standard sulfiding. At lower temperatures the second level decreases.

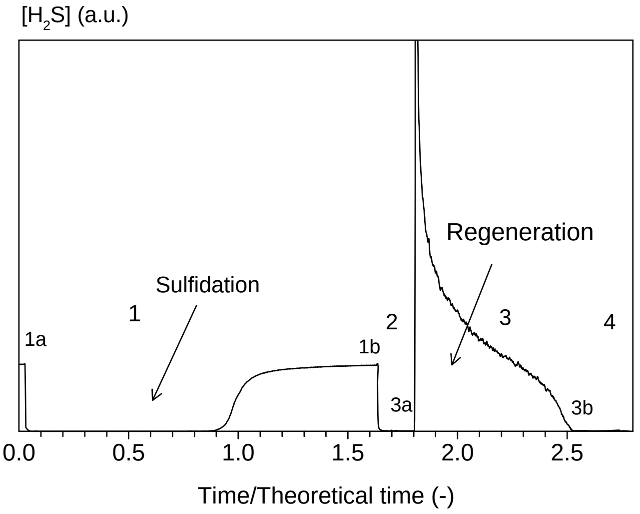

Fig. 8. Typical curves for isothermal sulfiding and regeneration at 1123 K (MW36). Co-current regeneration with steam in a fixed bed reactor. (Theoretical sulfiding time is time needed to sulfide all the manganese present with the chosen feed composition. Hereby an S/Mn equilibrium ratio of 1 is taken.) The regeneration profile with SO_2 regeneration is similar. The product is in that case S_2: (1) sulfiding; (2) flushing; (3) regeneration; (4) flushing (1a, 1b and 3a, 3b are feed signals before and after sulfiding and regeneration).

3.2.2. *Regeneration with SO_2, SO_2/O_2 or O_2*

Fig. 9 shows typical SO_2 concentration profiles during regeneration with SO_2 at different temperatures. Initially, a large part of the SO_2 is absorbed, after which the absorption tails off and reaches zero if all sulfur is removed from the acceptor. Elemental sulfur is formed as regeneration product, which is captured at the end of the reactor by condensation. This sulfur is bright yellow and does not contain significant contamination.

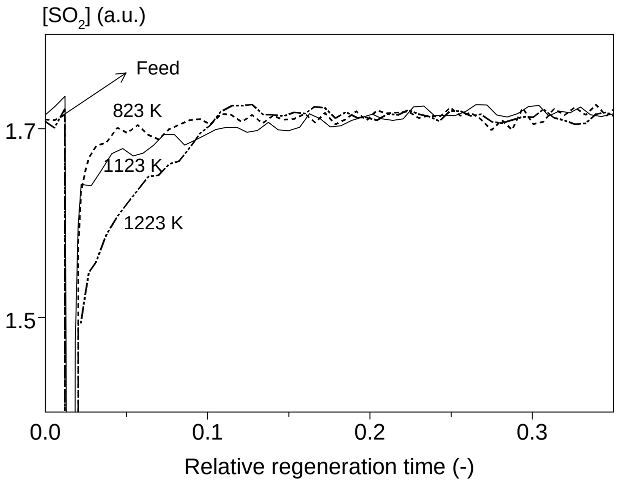

Fig. 9. Typical SO_2 absorption profiles during regeneration with SO_2 at different temperatures. (Relative regeneration time is the regeneration time/time need for complete sulfiding with 1 vol.% H_2S in the feed. Hereby a S/Mn of 1 is taken.) The SO_2 consumption is assumed to represent the S_2 production.

Table 2
Amount of sulfur recovered as elemental sulfur after regeneration with 50 mol% SO_2

Sample	Sulfiding	Regeneration	S recovery (%)
P21	Standard	SO_2	100
	Simulated coal gas	SO_2	95
P33	Standard	SO_2	99
	Standard	SO_2/O_2[a]	94

[a] 1.5 vol.% O_2.

At different temperatures all samples show the same initial SO_2 absorption, but the remainder of the absorption is strongly dependent on the temperature. At 1223 K the relative regeneration time is typically around 0.15 of the absorption time, while at 1123 K it is 0.3. At 823 K it is much longer and the exact time could not be determined.

Table 2 shows the sulfur production during regeneration of two samples. Sulfiding and regeneration results in a 94–100% recovery of the absorbed sulfur as elemental sulfur. The observed deviation from 100% is probably due to an inaccuracy in the working procedure and, in the case of O_2 addition, to partial conversion of the absorbed sulfur to SO_2. No S_2O could be observed.

3.2.3. *Steam regeneration*

In Fig. 8 steam regeneration is included. It starts with a sharp and high H_2S production peak, after which the production tails off slowly. When almost all sulfur is removed the H_2S production quickly drops to zero. The shape of the inversed SO_2 adsorption peak with SO_2 regeneration is comparable to the H_2S production peak. At 1123 K steam regeneration is (after correction for concentration differences) about two times slower than SO_2 regeneration.

3.2.4. *Acceptor capacity*

A typical sulfur uptake capacity[3] for isothermal absorption and regeneration (in temperature steps from 673 to 1273 K and back to 673 K) is depicted in Fig. 10. At all temperatures the same sample is used and at each temperature two cycles are performed. The acceptor capacity increases strongly from 873 to 1123 K, and stabilizes. At the maximum of the curve the S/Mn ratio is around one. Going back from 1273 to 673 K the same trend in the opposite way is observed. Below 1123 K, however, the sulfur uptake is less than the first measured capacity. This difference increases with decreasing temperature. At 673 K the capacity is even three times lower than the initial capacity at that temperature.

The uptake acceptor capacity for all samples increases almost linearly with the manganese loading (@1123 K; [7,8]). At a Mn loading of 36 wt.% the uptake capacity is about 20 wt.% sulfur. No significant difference has been observed between the different support types. With lower Mn loadings the S/Mn ratio increases with a few percent.

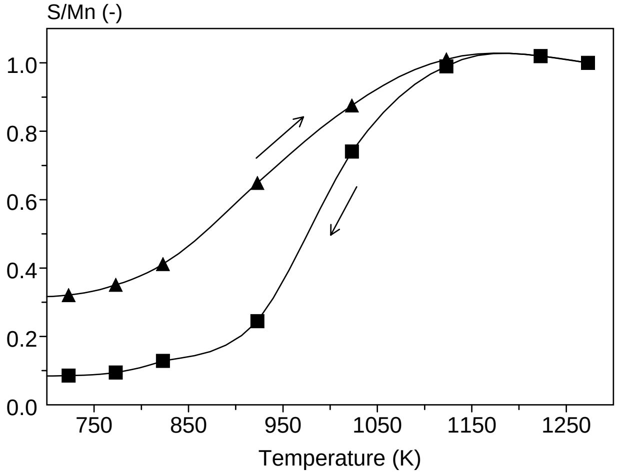

Fig. 10. Typical sulfur uptake capacity expressed in molar S/Mn ratio. Cycles from 723 to 1223 K are indicated with triangle (▲) and the cycles back to 723 K with square (■) (P12 samples).

3.2.5. *Capacity development and mechanical stability*

The acceptor sulfur uptake capacity as function of the number of cycles with standard sulfiding and standard SO_2 and steam regeneration is illustrated in Fig. 11a for a typical sample (MW36). During the first cycles the capacity, expressed in S/Mn ratio, decreases from 1.2 to 1. After this initial reduction hardly any further reduction is observed during the following 100 cycles.

In the same figure a test (35 cycles) with simulated coal gas shows similar results with MW40. The initial reduction is less pronounced and the relative capacity is about 10% lower. No coke formation is observed during these tests.

The effective capacity[4] during this experiment is around 75% of the theoretical maximum capacity ($S/Mn = 1$). During sulfiding of another sample (P36) with simulated coal gas a somewhat lower effective capacity was measured; 68% of the maximum capacity.

Cycling tests with standard sulfiding and standard SO_2 regeneration are shown in Fig. 11b. Similar to the other experiments P21 shows practically no reduction. The capacity of P36 declines about 20% during 40 cycles. Addition of a small amount of oxygen, 1–5%, to the regeneration gas did not lead to a significant better regeneration performance. Only with 8% of O_2 P36 was fully recovered. After regeneration with oxygen or SO_2/O_2 XRD showed that a part of the manganese on the acceptor is present as MnO.

No mechanical damage was observed for any of the tested samples after prolonged operation. The washcoat

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[3] The acceptor capacity is based on the total amount of H_2S absorbed and not on a certain breakthrough criterion. For reasons of convenience it is expressed as S/Mn ratio.

[4] Uptake capacity using a breakthrough criterion of 100 ppm H_2S at the exit of the sorbent bed.

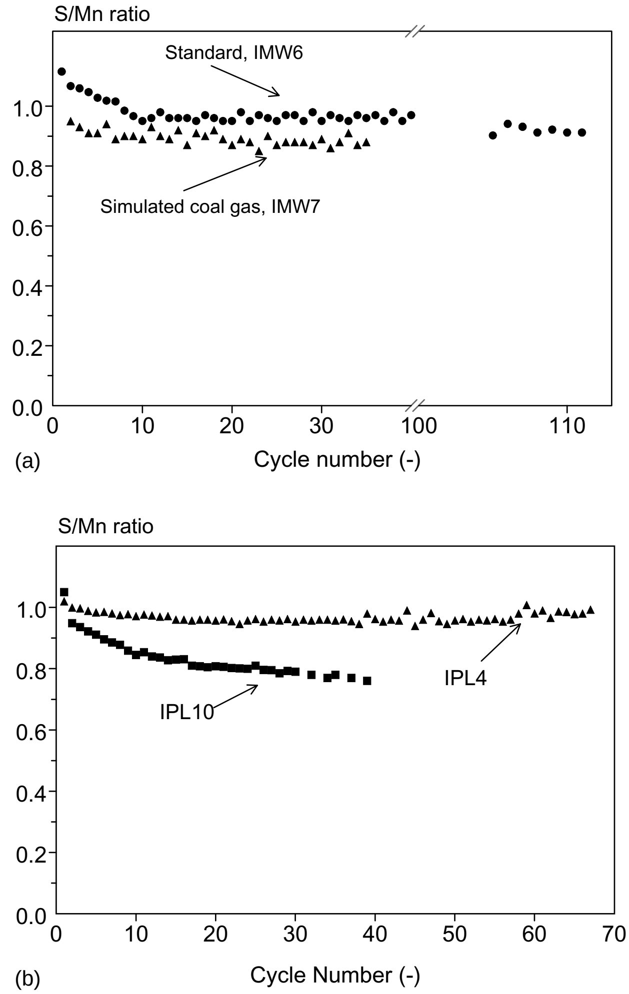

Fig. 11. (a) Capacity development during subsequent sulfiding and regeneration with steam for MW36 (IMW6) and MW40 (IMW7). MW40 is sulfided with a simulated coal gas. (b) Capacity development of P21 (IPL4) and P36 (IPL10) during subsequent sulfiding and regeneration with SO_2.

layer on the washcoated samples was still intact. Generally, the mechanical strength of washcoated samples, both before and after isothermal cycles at 1123 K, was higher than for the pure γ-alumina samples. This was "measured" by crushing some fresh and sulfided samples in a mortar.

4. Discussion

From the results presented it becomes clear that the developed acceptor for the desulfurization of dry coal gas is a rather complex system. Several chemical compounds are present in the solid phase, and both crystalline and amorphous phases co-exist. These components and phases behave differently under sulfiding and regeneration conditions. The resulting observed integral bed behavior can be understood if the separate contributions to this behavior are identified.

4.1. Characterization

The acceptor for dry coal gas desulfurization typically contains between 32 and 40 wt.% Mn. The crystals in these samples still have a relatively small size (<20 nm; Fig. 7) and can be fully sulfided and regenerated above 1073 K.

$MnAl_2O_4$ contains 31.7 wt.% Mn. This corresponds with the observation that formation of MnO occurs during regeneration if the amount of Mn in the sorbent is higher. The dispersion of the MnO phase is very high when a few percent overstoichiometric Mn is present. MnO in a sample which contained 35 wt.% Mn is only detected with TEM/EDX and not by XRD because of the small crystals. Thermodynamically, MnO is relatively insensitive to H_2O if it has to convert to MnS. It, therefore, enhances the desulfurization performance (depth) of the acceptor, especially in an H_2O containing atmosphere. The amount of MnO should preferably not be higher than the amount needed to obtain the desired concentration of H_2S in the cleaned gas. As shown in Fig. 4 the bulk thermodynamics for regeneration with SO_2 or H_2O are unfavorable and would require extra regeneration gas. Alternatively, addition of a few percent of oxygen to the regeneration gas may, theoretically, solve this problem.

The most important sorption and regeneration reactions that take place are given below. For a complete overview of the reactions the reader is referred to [7,8] and for a complete overview of the sulfiding mechanisms the reader is referred to [6,8,11].

- *Sulfiding*

$$MnO + H_2S \rightarrow MnS + H_2O \tag{6}$$

$$MnAl_2O_4 + H_2S \rightarrow MnS + \gamma\text{-}Al_2O_3 + H_2O \tag{7}$$

- *Regeneration*

$$MnS + 0.5SO_2 \rightarrow MnO + 0.75S_2 \tag{8}$$

$$MnS + Al_2O_3 + 0.5SO_2 \rightarrow MnAl_2O_4 + 0.75S_2 \tag{9}$$

4.2. Acceptor performance during isothermal cycles

The results show that a manganese-based sorbent can be made which is a good acceptor for high temperature desulfurization of dry coal gas. Especially, the high capacity combined with high stability and direct sulfur production is unique and not been reported for any sorbent before.

The sulfiding performance with different samples and under varying conditions is discussed below.

4.2.1. Desulfurization depth

Impregnated samples with a loading between 32 and 40 wt.% Mn appear to be good acceptors for dry hot gas desulfurization. If no or little water is present in the feed the sorbent can reduce the amount of H_2S to a level between 5 and 50 ppm (at 1123 K; Fig. 8). Also the desulfurization of simulated coal gas down to a level between 10 and 50 ppm H_2S is satisfactory assuming a desulfurization down to 100 ppm is required. This desulfurization level is in accordance with thermodynamical calculations for bulk MnO which predict a removal down to 40 ppm.[5]

4.2.2. Regeneration

Regeneration of sulfided acceptors with H_2O, SO_2, O_2 or a mixture of SO_2 and O_2 is possible. Especially the good results obtained with SO_2 regeneration are interesting because of the production of elemental sulfur. The different regeneration experiments are discussed below.

4.2.2.1. SO_2 regeneration. Regeneration with SO_2 is successful at temperatures above 873 K. Below that temperature sulfate formation occurs which results in H_2S release during sulfiding. Direct formation of sulfur takes place and the mass balance indicates that the conversion to S_2 is near to 100% (Table 2). Thermodynamic calculations predict (Fig. 6) that around 10% of the regeneration products are S_2O. Apparently, no or less S_2O is formed than thermodynamically predicted. This will be a point for future investigations.

The regeneration time using SO_2 is two times shorter than with H_2O regeneration (at 1123 K; Figs. 8 and 9). This is in accordance with calculations which predict that regeneration of MnS on Al_2O_3 at high temperatures is more favorable with SO_2 than with H_2O (Fig. 5), i.e. the driving force for reaction is larger which consequently results in faster regeneration.

The regeneration time is a function of the regeneration temperature (Fig. 9) and the manganese loading. Three aspects are important with respect to the regeneration time. The $[SO_2]/[S_2]$ equilibrium ratio for $MnAl_2O_4$, the relative amount of surface sites and the presence of Mn which has to be regenerated towards MnO.

Surface sites are regenerated fast compared to bulk sites. This results in high S_2 concentrations in the regeneration gas. The initial high S_2 peak is ascribed to surface sites. The height of this peak is directly related to the amount of sulfided surface sites.

Regeneration of samples with a high manganese loading requires a longer regeneration time because of the formation of MnO. This is thermodynamically less favorable than the formation of $MnAl_2O_4$ (high $[SO_2]/[S_2]$ ratio; Figs. 4 and 5).

The $[SO_2]/[S_2]$ exit level ratio decreases strongly with increasing temperature, Fig. 9. This trend is also predicted by the thermodynamic calculations, see Figs. 4 and 5. A decrease in diffusion limitation with increasing temperature may also play a role.

The direct production of elemental sulfur during regeneration with SO_2 is in most cases preferred over the production of SO_2 or H_2S. Regeneration of MnS to MnO with SO_2 or H_2O is difficult and requires larger amounts of regeneration gas. Therefore, in practical applications some of the material might preferably be regenerated with oxygen. However, regeneration with a SO_2/O_2 mixture results in relatively more severe sintering (Table 2). Furthermore, it was observed that MnS on γ-Al_2O_3 after regeneration with diluted O_2 contained a relatively large amount of MnO. Possibly, the formation of MnO instead of $MnAl_2O_4$ accelerates sintering. It is expected[6] that regeneration of the remaining MnS with diluted O_2 (typically 2–3%) after regeneration with SO_2 is a more successful method, and will result in less sintering compared to direct addition of oxygen to SO_2. An advantage of direct addition of O_2 to SO_2 is that the exothermal reaction with oxygen can compensate the endothermal regeneration with SO_2. High oxygen concentrations should be avoided as it leads to unacceptable temperature rise in the acceptor bed and requires additional cooling. Possible process schemes for regeneration with SO_2 and O_2 are depicted in Figs. 13–15.

4.2.2.2. Steam regeneration. The main product during regeneration of sulfided samples with H_2O is H_2S. Above 1123 K besides H_2S some SO_2 and S_2 is also formed. This has been predicted by thermodynamic calculations and has been observed during experiments [7,8]. The observed regeneration behavior can be explained in a similar way as described above for the SO_2 regeneration.

4.2.3. Optimal operation temperature

The highest capacity is obtained between 1123 and 1223 K. Below 1123 K the capacity decreases (Fig. 10). Above it was argued that the optimal operation temperature for desulfurization was at temperatures between 1000 and 1200 K. The highest uptake capacity is thus obtained around the optimal operation temperature which is, of course, satisfactory. The low sulfur uptake capacity at 723 K, reduced after heating towards 1273 K can be explained by surface loss caused by the sintering of the sorbent since at low temperatures only the surface sites can be sulfided [17].

4.2.4. Sulfur uptake capacity

The sulfur uptake capacity of the different samples is high and increases to 20 wt.% sulfur at a manganese loading of 36 wt.%, much higher than most existing regenerable sorbents ([1,10,12,15,19], etc.)

The S/Mn ratio decreases a little with increasing Mn loading. This may be explained by the formation of an increasing amount of (large) irregenerable MnS crystals with increasing Mn loading.

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[5] Assuming a $[H_2O]/[H_2S]$ equilibrium ratio for MW40 and P36 of 225 and a K_{eq}^{b} of 1 for the water gas shift reaction.

[6] Only the sites most difficult to regenerate need oxygen. The other sites should preferably be regenerated with SO_2. If oxygen is added from the beginning the whole recrystallization process will be faster. In general, a very fast recrystallization process will lead to sintering and should be avoided if not necessary.

4.2.5. Optimal manganese loading

A high manganese loading and thus, for impregnated samples, a high sulfur uptake capacity is not necessarily the optimal manganese loading. The maximum capacity is always lower than the practical capacity (=capacity which can be used in an industrial desulfurization process).

According to a previous work [17] the optimum performance is reached with a manganese loading of 8 wt.% at 873 K. This resulted in a practical sulfur uptake capacity between 0.5 and 1.5 wt.% sulfur. Higher loadings did not result in a higher capacity at this temperature and it was believed that, although higher temperatures increased the S/Mn ratio, excessive sintering during prolonged operation would destroy the acceptor capacity.

Indeed, sintering and reduced uptake at low temperatures is observed after cycles at high temperatures, see Fig. 10. However, for desulfurization at high temperatures the following was overlooked: solid state diffusion is an activated process and, as a consequence, with increasing temperature, diffusion in the solid phase, at least partly, compensates the decrease in capacity by the loss in surface area. The formation of an amorphous phase at high temperatures may also enhance the reaction rate as diffusion in an amorphous phase is, in general, relatively fast. Above 1100 K the loss in surface area is completely compensated by a higher solid state diffusion rate (Fig. 10). At low temperatures a high surface area is still important since the capacity is then directly related to the surface area, and thus always relatively low.

The current manganese-based sorbent has been designed for desulfurization of dry coal gas (0.4–2 vol.% H_2O) down to a level of below 100 ppm H_2S. At 1123 K bulk $MnAl_2O_4$ can remove about 90% of the H_2S from our simulated dry coal gas.[7] The remaining 10% should be removed in an alternative way. Surface sites can remove H_2S to a very low level. This has been shown in, e.g. Fig. 8 and by Wakker et al. [17] and Soerawidjaja [14]. Also MnO can remove H_2S to a sufficient low level if the water content in the feed is relatively low; <2.5 vol.% after the WGS reaction. Thus, if sufficiently available, MnO and surface sites remove the H_2S which is not absorbed by $MnAl_2O_4$. With a water concentration >2.5 vol.% in the feed, two break trough levels can be observed which correspond to the thermodynamic $[H_2O]/[H_2S]$ ratio (K^{b}_{eq}) of MnO and $MnAl_2O_4$, respectively. A disadvantage of MnO is that it is difficult to regenerate with steam or SO_2 after sulfiding. The amount of MnO should, therefore, be minimized. Sulfided surface sites are easy to regenerate. Their availability is, however, limited. It has been shown in Table 1 that the surface area at 1123 K stabilizes around 14 m^2/g_{active}. The maximum absorption capacity at 1123 K of surface sites is, therefore, only about 1 wt.% sulfur. Theoretically, 2–4 wt.% MnO is required additionally. As $MnAl_2O_4$ contains 32 wt.% Mn the optimal Mn loading of a sorbent is around 35 wt.% Mn. To avoid excessive usage of SO_2 additional regeneration with oxygen may be useful, especially for samples with a high amount of MnO. Different process options are discussed below.

4.2.6. Practical sulfur uptake capacity

During sulfiding the full capacity of the sorbent cannot be used because the sulfiding is stopped if the thermodynamic $[H_2S]/[H_2O]$ concentration ratio is reached and the surface sites are occupied. For a feed with 2% H_2O and 0.7% H_2S the practical sulfur uptake capacity during sulfiding with simulated coal gas is with 14 wt.% sulfur, still high.

4.2.7. Acceptor stability, mechanical strength and influence of impurities in feed

The stability tests indicate that the sorbents have a stable performance during prolonged operation (40–110 cycles; Fig. 11). Little or no capacity loss during the first cycles (<20%) has been observed. An exception is P36; if it is regenerated with SO_2 the loss is higher than 20%. Possibly, the regeneration with SO_2 of overstoichiometric MnS leads to the formation of relative large crystals which are difficult to regenerate after being sulfided again. See also discussion in Section 4.2.2.

Besides H_2S the coal gas contains other impurities like dust, HCl, HF and alkali metals. As shown in Fig. 3, theoretically, HCl and HF are also taken up by $MnAl_2O_4$. These components cannot be removed with SO_2 but they can be removed relatively easily with H_2O. This difference can be beneficial during regeneration of the sample. HCl or HF will not be released during SO_2 regeneration and thus the product gas will not be contaminated with these components. In a practical application the sorbent should be treated with steam after a number of cycles to remove the absorbed HCl and HF. Some deactivation might occur by volatilization of $MnCl_2$ at 1123 K. The amounts are, likely, small because of the high boiling point of $MnCl_2$. Further experimental work is needed to demonstrate this concept.

Also alkali metals have to be removed from the coal gas. No data are available on the influence of these metals on the manganese sorbent. Removal of alkali metals at high temperatures, up to 1223 K, can be performed with another sorbent, e.g. with “Fullers earth” as described by Schultz [13].

4.3. New process proposal for coal gas cleaning

In this section the implementation of high temperature gas cleaning in a process is discussed conceptually.

It has been shown that the application of the developed manganese-based sorbent is feasible for high temperature desulfurization of dry coal gas. A schematic representation of the sorbent is shown in Fig. 12. Theoretically, also the regenerative removal of HCl and HF is possible with this sorbent. An interesting feature is that the regeneration of the sulfided sites can occur independently from the regeneration of the chlorinated and the fluorinated sites. While

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[7] 2% H_2O and 0.7% H_2S; $K_{WGS} \approx 1$, $[H_2O]/[H_2S]$ equilibrium ratio = 1.

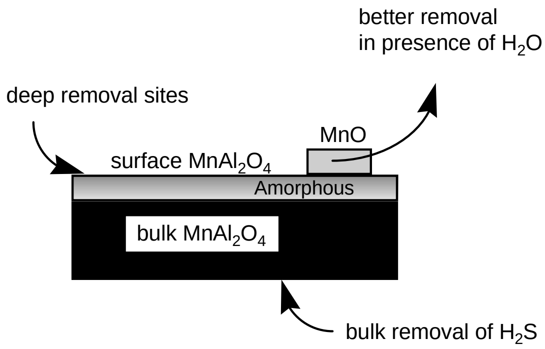

Fig. 12. Schematic representation of the manganese-based sorbent developed. The combination of three types of sorption "sites" ensures a good desulfurization depth and a high capacity. Besides the direct sulfur production during regeneration the applicability without significant deactivation up to very high temperatures is an attractive characteristic.

SO_2 regenerates the sulfided sides it does not regenerate the other sites. These sites can be subsequently regenerated with steam. Besides the removal of the above-mentioned components, a small amount of alkali metals also have to be removed from the fuel gas. Absorbents have been reported, which absorb alkali metals very efficiently, at very high temperatures also, e.g. Fullers earth (Schultz [13]). However, no regeneration of these sorbents is possible.

Fig. 13 shows a proposal for a new gas cleaning process at high temperature. The gas leaving the gasifier is not cooled and flows directly to the cleaning section. First the alkali metals are removed in a fixed bed absorber. H_2S, COS, HCl and HF are removed in, e.g. a rotating monolith reactor as described by Bakker et al. [3,4,8]. Regeneration of the sulfided sites occurs with SO_2 or with a mixture of SO_2 and O_2. The other sites are regenerated with steam after the regeneration of the sulfided sites to minimize contamination with H_2S. The regeneration products are pure elemental sulfur, and steam with HCl and HF. After cleaning the gas flows (preferably) without heat exchange to the conversion section.

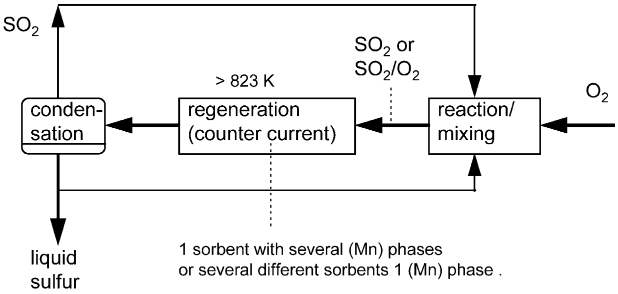

Fig. 14. Process scheme for the regeneration of the sulfided sites.

The main differences with the "low temperature gas cleaning process" are:

- No syngas cooler and reduce other heat exchange equipments.
- No separate Claus plant is needed.
- The inlet temperature in the gas conversion unit is equal to the gas outlet temperature of the cleaning section. This unit may be new generation gas turbine, an SOFC, or another device.

In principle, this design results in a lower capital cost, a higher efficiency, and less complex process operation.

4.3.1. Regeneration of the sulfided sites

In Fig. 14 the simplified regeneration process is depicted. It has been discussed above that the sorbent can be regenerated in several ways to obtain elemental sulfur as regeneration product, including regeneration with SO_2, SO_2 in combination with a small amount of O_2, or SO_2 followed by SO_2 with a small amount of O_2. The addition of oxygen improves the regeneration of sites which are difficult to regenerate. On the other hand, experiments indicated that direct addition of oxygen lead to some deactivation of the easy to regenerate sites. The preferred regeneration method is, therefore, the regeneration of easy to regenerate sites with pure SO_2, followed by regeneration of the difficult to regenerate sites with a SO_2/O_2 mixture. The SO_2 can be

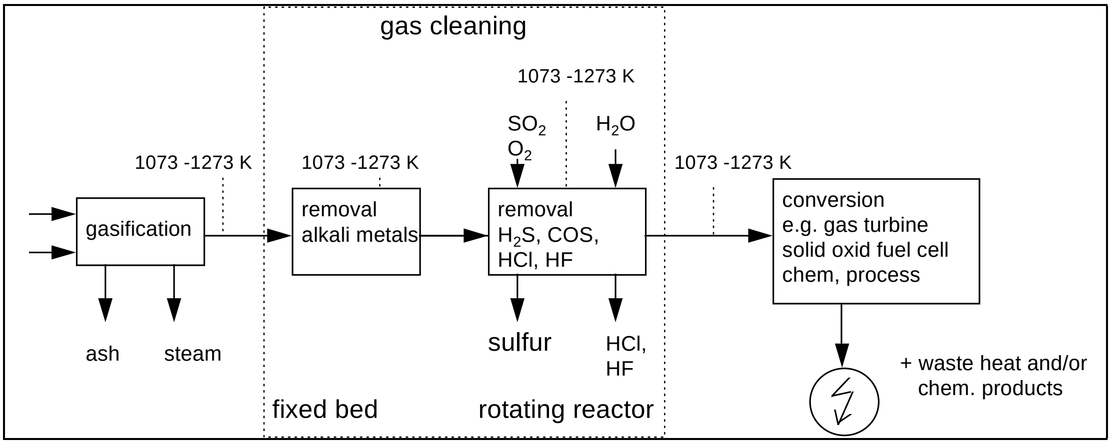

Fig. 13. Simplified representation of the proposed coal gas cleaning and conversion process.

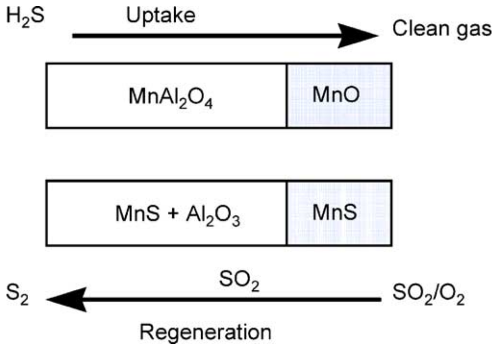

Fig. 15. Operation principle of a two sorbent desulfurization process in a rotating or fixed bed reactor.

obtained by the oxidation of a small amount of the produced sulfur.

The regeneration gas leaving the (rotating) reactor contains a mixture of SO_2 and S_2. The SO_2 is reused and most of the S_2 is condensed from this mixture. To obtain liquid sulfur the condensation temperature should be between 400 and 700 K. After condensation, the remaining SO_2 is reheated to the required inlet temperature of the regeneration section. The required heat can be partly supplied by the exothermic oxidation of sulfur.[8] In the process scheme part of the liquid sulfur is fed back to an oxidation section. The sulfur is also partially supplied via the gas phase with SO_2.

The developed sorbent contains different manganese phases to ensure a good capacity and desulfurization depth. Another option for effective desulfurization is the use of different sorbents, e.g. MnO in combination with $MnAl_2O_4$, see Fig. 15. During sulfiding $MnAl_2O_4$ captures the bulk of the H_2S while MnO captures efficiently the remainder. During regeneration, in the counter current mode, MnS is efficiently converted to MnO with O_2 from an O_2/SO_2 mixture. The remaining SO_2 regenerates the MnS on Al_2O_3 to $MnAl_2O_4$. For effective desulfurization with different absorption materials, e.g. a consecutively operated fixed bed or rotating reactor should be used; preferably loaded with monolith shaped sorbents. In a fluidized bed the use of two or more separate sorbents will not be effective.

5. Conclusions

- A regenerative high capacity manganese aluminate-based sorbent for high temperature desulfurization has been developed.
- Regeneration with SO_2 directly yields elemental sulfur.
- The sorbent is stable for at least 110 cycles.
- The high stability and capacity in combination with direct sulfur production is unique.
- The sorbent can possibly be used for simultaneous regenerative removal of HCl and HF.
- A new dry coal gas high temperature process concept is proposed with direct sulfur formation, eliminating the Claus plant.

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