Hot gas desulphurisation with dolomite sorbent in coal gasification

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ABSTRACT

Keywords:
Gasification
Desulphurisation
Dolomite
Coal

Gasification technologies are among the most promising electrical power generation options both from an environmental and efficiency point of view, as they allow efficient, environmentally-friendly use of national coal, as well as other carbonaceous materials mixed with coal, including high sulphur by-products.

During gasification, sulphur is converted mainly into H$_2$S and secondly into COS, and control of these has been researched using several H$_2$S adsorbents. The aim of this paper was advanced removal of these compounds.

Dolomite, which reacts with H$_2$S to yield calcium sulphide, was chosen from among several earth-alkaline compounds for research due to its properties and low cost in reducing the presence of H$_2$S in coal gasification.

Tests were carried out using dolomite from Granada, Spain, with this sorbent used without blending and with amounts of 100 g and 150 g in each test. The dolomite was sulphurised using a mixture of gases that simulates the gasification gas.

The influence of sulphurisation conditions such as gas velocity, bed length, grain size, gas temperature, and gas composition were investigated. The solid products obtained were characterised by X-ray diffraction and chemical analysis.

The behaviour of COS that normally accompanies H$_2$S in gasification gases was investigated and found to follow a breakthrough curve similar to H$_2$S, with equilibrium existing between the COS destroyed due to reaction with hydrogen and by hydrolysis and the COS formed by reaction of CO$_2$ with H$_2$S. Hence, its content in outlet gases is a function of the composition of this gas, especially in terms of CO$_2$, H$_2$S and H$_2$O.

The accelerating effect of sulphurised dolomite on the rate of the reverse water-shift reaction was demonstrated.

1. Introduction

In the gasification of coal or blends with other alternative fuels, sulphur is mainly present in the gas as hydrogen sulphide. This sulphur compound must be removed prior to gas combustion to comply with legislation and especially to avoid damage to the turbines. In the chemical industry, the presence of H$_2$S leads to larger corrosion problems (pipes, compressors, etc.) and also problems with some catalysts. The scrubbing of sulphur from the gas stream has been widely studied using different agents, such as the amines used by Elcogas IGCC in Spain; however, this option requires a decrease in gas temperature that causes the inherent energy losses.

Some sorbents that allow H$_2$S to be removed at high temperatures have been previously investigated; these include diverse metal compounds. Sorbent regeneration without significant degradation during a certain number of cycles is extremely important. Several Zn compounds, some Mn and Cu compounds and blends and some Fe compounds have also been studied. The main problem is the sufficient duration of cycles without degradation. One very cheap oxide, CaO, that does not need to be reused has also been studied. The main sources are two abundant minerals, calcite and dolomite. The direct addition of this oxide or the calcite in the gasification bed for coal gasification or the gasification of other alternative fuels has been investigated not only to clean the gas, but to produce hydrogen and also the absorption of H$_2$S in the oxides to remove them from the gas.

Calcium oxide is effective in adsorbing H$_2$S from the gasification gases according to the reaction:

$$H_2S + CaO \rightarrow CaS + H_2O(g) \quad \Delta H^0 = -59.2 \text{ kJ mol}^{-1} \quad (1)$$

but many studies with calcite or dolomite have been carried out on small samples in a thermobalance or differential reactor with 1 mg to 1 g. In other cases, larger amounts of absorbent have been used but mixed with silica grains to form a homogeneous
mixture of sorbent and silica to avoid improper random distribution of the gas flow and reduce errors in the longitudinal conversion of profiles as in articles with the aim of obtaining appropriate measures to develop mathematical models.

In the case of an industrial application it would be appropriate to apply the pure absorbent which is why this investigation was carried out in this way and the different behaviour investigated according to grain size and position in the absorbent column: at the top or at the bottom subjected to more mechanical pressure. Absorbent amounts of 100 g and 150 g that give bed lengths of 11.4 and 17 cm, respectively, were also used.

The absorbent chosen was dolomite as it works well under calcining (1123 K) and non-calcining conditions (1713 K) according to previous studied by Adanéz.

H₂S in the gasification gases is known to be accompanied by a certain proportion of carbonyl sulphide (COS) that when burnt, yields SO₂ according to the following reaction:

\[ \text{COS} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + \text{SO}_2 \quad \Delta H^0 = -552 \text{ kJ mol}^{-1} \]  

(2)

This reaction increases the SO₂ content of gases and increases the corrosive effect in gas turbines, gas motors, pipes and general industrial equipment and also increases SO₂ emissions. Therefore, it should be reduced. At Elcogas, for example, this is carried out by COS hydrosulphisation according to the following reaction:

\[ \text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2 \quad \Delta H^0 = -33.6 \text{ kJ mol}^{-1} \]  

(3)

H₂S is later eliminated by amine extraction.

There are various studies on COS hydrosulphatisation especially aimed at the development of new catalysts such as earth oxysulphides but that require operating at relatively low temperatures. However, the ability to reduce COS at high temperatures using the same approach as H₂S on earth alkaline sorbents would be of interest. This possibility has already been studied by Heesink but limited to lower temperature (up to 700°C) and with a very small amount of sorbent and that postulates the reaction:

\[ \text{CaO} + \text{COS} \rightarrow \text{CaS} + \text{CO}_2 \quad \Delta H^0 = -90 \text{ kJ mol}^{-1} \]  

(4)

Ishida also postulates the reactions:

\[ \text{CO}_2 + \text{H}_2\text{S} \rightarrow \text{COS} + \text{H}_2\text{O} \quad \Delta H^0 = +33.6 \text{ kJ mol}^{-1} \]  

(5)

\[ \text{CO}_2 + 2\text{H}_2\text{S} \rightarrow \text{CS}_2 + 2\text{H}_2\text{O} \quad \Delta H^0 = +68 \text{ kJ mol}^{-1} \]  

(6)

The proportion of COS to be expected will also depend on the concentrations of CO₂, H₂S and H₂O (reaction (5) is the reverse of (3)).

To achieve a reduction in H₂S and COS levels at very low values, some authors use Zn composites as absorbents that carry out desulphurisation over two stages, one to reduce the high level of H₂S at a low value, followed by another stage that uses an especially prepared absorbent with a high specific surface area.

In the present study, H₂S was contaminated with a small amount of COS (about 1% of the H₂S content) with the aim of investigating any decreases or increases under the test conditions, now operating with relatively large amounts of 100 g or 150 g of material. The contamination is sufficiently low so as not to decisively influence the principal sulphidisation reaction with hydrogen sulphide (1).

Another important reaction to consider is the reverse water-shift reaction, which influences the proportion of H₂ in the outlet gases, an important aspect if hydrogen is to be produced:

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H^0 = +41.1 \text{ kJ mol}^{-1} \]  

(7)

2. Experimental

All experiments were performed using a dolomite from the province of Granada, Spain, that presented an essentially theoreti-
Table 1
Granada dolomite analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Content%</th>
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<tr>
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<td>MgO</td>
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<tr>
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<tr>
<td>K₂O</td>
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</tr>
<tr>
<td>Na₂O</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Insoluble</td>
<td>0.20</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>47.53</td>
</tr>
</tbody>
</table>

Fig. 2. Thermogram of the dolomite used (— weight, -- temperature).

Fig. 3. Simplified chart of the system used. Dolomite at bottom position below a silica column.

3. Results and discussion

3.1. Absorption of hydrogen sulphide

3.1.1. Influence of grain size, gas velocity and relative position in the desulphurising column (top or bottom)

By operating as described in Section 2, virtually complete (98–99%) dolomite sulphidisation is obtained when the higher grain size of 2–2.5 mm was used, which would be the most difficult to sulphurise under different test conditions. Fig. 4 shows the X-ray diffraction of sulphurised dolomite, which contains no line of CaSO₄ or CaO, but rather only CaS (oldhamite) and MgO (periclase) lines.

Fig. 5 shows the breakthrough curves from various tests carried out at a gas velocity of 29.1 and 14.5 cm s⁻¹ and considering the case of dolomite at the bottom of the desulphurising column under more static pressure (tests 2, 3, 7, 9, 10 and 11; Table 2) and a test carried out with dolomite at the top of the column (test 6).

The H₂S concentration of the outlet gas has been plotted as a percentage with respect to the maximum output: 100% corresponds to approximately 20,000 ppm of H₂S, but not exactly as there are small variations due to a small variation in the proportions of outlet COS (see Section 3.2.).

To explain the influence of the gas velocity, it was observed that the curves (for the three grain sizes) carried out at lower velocity are shifted toward the right but approximately retained their shape, a finding that is consistent with previous studies [19]. This occurs because a lower gas velocity was used, which meant that the amount of H₂S introduced per time unit was lower and that more time was needed to reach a definite degree of saturation.
To explain the influence of grain size, it was observed that the curves corresponding to lower granulometries (0.4–0.5 mm) at the bottom have a flatter gradient than those corresponding to 2–2.5 mm at both gas velocities of 29.1 and 14.5 cm s\(^{-1}\). The tests with a grain size of 0.71 have an intermediate position. This shows that lower grain sizes result in greater grain packing in a compact bed of dolomite grains, thus creating preferential paths for the gas and delaying H\(_2\)S absorption. Therefore, under the conditions used, this means that a grain size of 2–2.5 mm will yield better results.

The effect of dolomite position can be observed by comparing the grain size of 0.71 mm with breakthrough curves at 29.1 cm s\(^{-1}\), one at the top and the other at the bottom. At the bottom position, the gradient is flatter. The 0.71 mm curve at top position can also be compared with the curve of 2–2.5 mm at the bottom position, both at 29.1 cm s\(^{-1}\): the curves are practically identical and have the shape of the breakthrough curves obtained by Adánez et al. (especially the curve for 0.71 mm) who used silica mixtures to obtain more uniform permeability and to adjust the mathematical models. Under the conditions used, the curves at the bottom with the shape most closely resembling the mathematical models are those corresponding to a larger grain size (2–2.5 mm), in contrast with [19].

### 3.1.2. Influence of temperature (850 °C, 900 °C or 950 °C)

Fig. 5 shows three curves for 100 g of sample (11.4 cm bed thickness) and 2–2.5 grain size, in bottom position sulphurising with 14.5 cm s\(^{-1}\) gas velocity, 2% H\(_2\)S and temperatures of 1123 K, 1173 K and 1223 K (test 11, 13, and 15, Table 2).

Almost no differences in curve shape and values were observed between sulphidisation temperatures of 1123 K, 1173 K and 1223 K (test 11, 13, and 15, Table 2).

### Table 2

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>Inlet gas (N(_2) balance gas)</th>
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<tr>
<td>Test</td>
<td>Material</td>
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<tr>
<td>1</td>
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<tr>
<td>2</td>
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</tr>
<tr>
<td>3</td>
<td>Dolomite</td>
</tr>
<tr>
<td>4</td>
<td>Dolomite</td>
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<tr>
<td>6</td>
<td>Dolomite</td>
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<td>7</td>
<td>Dolomite</td>
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<tr>
<td>8</td>
<td>Dolomite</td>
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<tr>
<td>9</td>
<td>Dolomite</td>
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<td>10</td>
<td>Dolomite</td>
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<td>11</td>
<td>Dolomite</td>
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<td>12</td>
<td>Dolomite</td>
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<td>15</td>
<td>Dolomite</td>
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<tr>
<td>16</td>
<td>Dolomite</td>
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<tr>
<td>17</td>
<td>Dolomite</td>
</tr>
<tr>
<td>18</td>
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<td>21</td>
<td>Silica</td>
</tr>
<tr>
<td>22</td>
<td>Silica</td>
</tr>
<tr>
<td>23</td>
<td>Silica</td>
</tr>
</tbody>
</table>
At the beginning of sulphidisation, when practically all \( \text{H}_2\text{S} \) is adsorbed, the equilibrium constant for the case of calcining conditions can be expressed as

\[
K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{S}}} = 1.13 \exp(7262/T).
\]

(8)

At the beginning of sulphidisation, when practically all \( \text{H}_2\text{S} \) is adsorbed and taking in account the water generated by this adsorption reaction (1) and the water generated by the reverse shift reaction (7), the \( \text{H}_2\text{S} \) values in equilibrium at 1123 K, 1173 K and 1223 K are 208, 278 and 361 ppm, respectively (when 2\% \( \text{H}_2\text{S} \), 18\% \( \text{H}_2 \), 6\% \( \text{CO}_2 \) and 10\% \( \text{H}_2\text{O} \) balanced with nitrogen are used). The higher the temperature, the higher the values of the \( \text{H}_2\text{S} \) concentration in equilibrium in accordance with the results presented.

These theoretical values are lower than the values observed for each set of parameters. Fig. 7 shows a plot of the theoretical value at 850 °C which clearly indicates the difference.

### 3.1.3. Influence of bed length

Figs. 6 and 7 also show this influence in some tests with a grain size of only 2–2.5 mm. In Fig. 6 the breakthrough curves of the test using 11.4 cm of bed length are grouped on the left side and those corresponding at 17 cm bed length are grouped on the right. There is a shift toward the right when bed length increases; this shift is independent of test temperature and occurs because a longer bed length means there is more solid to react and more time is needed to reach a particular conversion grade.

Fig. 7 contains a plot of the theoretical value of \( \text{H}_2\text{S} \) in equilibrium at 850 °C; this value is lower than the values observed at 850 °C (tests 11 and 12). The difference is greater in the case of 11.4 cm compared with 17 cm because there is more solid to react and more contact time between the gas and solid when 17 cm is used instead of 11.4 cm. This allows closer approximation to the theoretical value. Another conclusion is that even at the lower gas velocity used (14.5 cm s\(^{-1}\)), a 17-cm bed length is not enough to reach the theoretical value. Bed length is therefore an important parameter to narrow the gap between the potential results of a hypothetical industrial application and the theoretical values.

Fig. 8 also shows the influence of using a bed length of 11.4 or 17 cm under other conditions (tests 6, 8, 12 and 13; Table 2). Tests 12 and 13 (2.5-mm grain size, 14.5 cm s\(^{-1}\)) have been discussed previously and test 6 and 8 have the same grain size (0.71 mm), gas velocity (29.1), position (top) and temperature (850 °C). In test 8 (17 cm), the curve is shifted toward the right hand when compared to test 6 (11.4 cm bed length) and both curves have a similar gradient. Thus, this shift due to the bed length is produced with different grain sizes, gas velocities, sample positions in the desulphurising column, and temperatures.

Fig. 9 shows the initial part of the curves extended. The \( \text{H}_2\text{S} \) content of the outlet gases is lower with a longer bed length when compared with tests under other similar conditions, but with a shorter bed length.

### 3.1.4. Influence of \( \text{H}_2\text{S} \) concentration in initial gases

Fig. 10 shows an extension of the initial area of the breakthrough curves for several tests that jointly show tests performed
3.1.5. Influence of composition of gas to be desulphured

trained flow or higher in other cases. During sulphidisation, reac-

tration and therefore the reaction can produce results approaching

S to react at any instant and relatively

umn because there is less H

2

except for H

S concentration and test 18 has the same operating

parameters as test 12 except for H

S concentration. Tests 17 and

2

18 performed with a concentration of 0.4% H

2

have curves below

18). Test 17 has the same operating parameters as test 10
except for H

2

concentration, tests (Table 2) 10 (A, 11.4 cm, 850 °C, 14.5 cm s

1

-g.v.) and 13 (•, 2 mm, bottom position, 14.5 cm s

1

-g.v.), 11 (•, 11.4 cm, 850 °C, 29.1 cm s

1

-g.v.); 12 (A, 850 °C, 17 cm, 14.5 cm s

1

-g.v.) and curve of% CaS conversion (•).

with 2% H

2

(tests 10,11,12,13,14) and tests with 0.4% H

2

(tests 17 and 18). Test 17 has the same operating parameters as test 10
except for H

2

concentration and test 18 has the same operating

parameters as test 12 except for H

2

concentration. Tests 17 and

18 performed with a concentration of 0.4% H

2

have curves below the others. The decrease in the H

2

concentration of the inlet gases produces lower saturation at each point of the desulphurant column because there is less H

2

S to react at any instant and relatively more free active points at any instant than at a higher H

2

concentration and therefore the reaction can produce results approaching the theoretical values.

The curves for tests 17 and 18 have a nearly flat initial stage that is practically identical; however, test 18 is slightly below test 17 due to longer bed length and lower velocity (Δ: 17 cm, 14.5 cm/s, instead of □: 11.4 cm, 29.1 cm s

1

).

3.1.5. Influence of composition of gas to be desulphured

Given the principal sulphurisation reaction (1), the presence of steam will obviously be one of the factors controlling the balance of the reaction.

In gasification gases, the presence of steam is normally 10% or
higher and the presence of CO

2

may be around 3% in the case of entrained flow or higher in other cases. During sulphidisation, reac-

tion (1) also yields water, especially in the initial stages in which nearly all H

2

S reacts, which modifies the equilibrium.

When only nitrogen, hydrogen and H

2

S (2%) are used (test 7, Fig. 11), only water generated in reaction (1) will be present (approximately 2%). This is when the lowest H

2

S values (Δ) are obtained in the outlet gases. Fig. 11 contains a comparison of tests 7, 10, 11 and

16. When 6% of CO

2

is introduced with no water (test 16) in such a way that the water present is that generated in reaction (1) plus that generated by reaction (7), there is more water (approximately 5.5%) and higher results are obtained than in the previous case but lower than when 10% of water is introduced, test no. 10 and test no. 11.

3.1.6. Conversion of calcium content in dolomite according to H

2

S concentration in outlet gases and application to the case of 400 ppm of H

2

S

Fig. 12 shows the curve of outlet H

2

S normalised to 100% corresponding to test 12, (Table 2) (150 g dolomite, 14.5 cm s

1

-gas velocity, 850 °C and grain size of 2-2.5 mm).

According to chemical analyses at the end of the test, CaO conversion to CaS was about 99%; therefore, the area over the curve in the plot represents the amount of H

2

S used to convert practically all CaO into CaS (99%). This area can be calculated by integration of the amount adsorbed (20,000 ppm - H

2

S content at each point) at each instant between 0 and the final time.

When integrating between 0 and each time point, the area represents the H

2

S amount adsorbed up to that time. If this is ex-
pressed as a percentage of total area, then the percentage of H$_2$S absorbed with respect to the total is obtained; this is equivalent to a conversion percentage of disposable CaO at the time considered and at the respective outlet H$_2$S concentration. When integrating at all time points corresponding to the points of the curve, the curve that represents the percentage of CaO conversion is obtained (■). As a result, this curve is also equivalent to the percentage conversion of Ca into CaS.

As observed initially, there is a practically linear growth that later tends towards a total of 100%.

For any particular outlet H$_2$S concentration, the time can be determined from the H$_2$S breakthrough curve. This time allows the percentage of calcium conversion to be determined from the other curve.

Table 3 shows the Ca conversion for tests carried out with samples of 2–2.5 mm for a concentration of 400 ppm of H$_2$S in the outlet gases.

Furthermore, under these conditions the concentration in the outlet gases is about 5 ppm of COS (see Section 3.2).

Table 3 shows how the percentage of calcium converted increases as gas velocity decreases (test 11 as compared with test 10), bed length increases (test 12 as compared with test 11, test 14 as compared with test 13, and test 18 as compared with test 17), initial H$_2$S decreases (test 17 as compared with test 10 and test 18 as compared with test 12) and steam concentration in the initial gas decreases (test 16 as compared with test 11).

3.2. Behaviour of COS

A total of 176 ppm of COS was introduced with the mixture of 2% H$_2$S.

When a silica bed was used (test 19) in the same way as dolomite at 850 °C and the gas contains only 2% H$_2$S, 18% H$_2$ and 176 ppm of COS (balanced to 100% with CO$_2$ and steam-free N$_2$) and the same conditions are used as in a dolomite sulphurisation test, then the COS value at the outlet drops to approximately 1.5 ppm (already borderline for precision measurements using a gas chromatograph). Similarly, the H$_2$S content increases by approximately the same amount of COS, considering the relative errors to detect 176 ppm in 20,000. This shows that the following reaction is occurring:

$$\text{COS} + \text{H}_2 \rightarrow \text{H}_2\text{S} + \text{CO} \quad \Delta H^\circ = +7.4 \text{ kJ mol}^{-1}$$  \hspace{1cm} (9)

A similar reaction occurs when dolomite is sulphurised with the mixture of H$_2$S, H$_2$ and N$_2$ without adding CO$_2$ or water (as in test 7). Fig. 13 contains the results (Δ) of this test, which shows even when the sample is totally sulphurised, the outlet COS concentration is also practically 1.5 ppm (other curves under other conditions are shown in this figure).

When silica is used (test 20, Table 2) and a mixture of 6% CO$_2$, 18% H$_2$, 10% H$_2$O and 2% H$_2$S (balanced to 100% with N$_2$) at 850 °C is passed, as used for most sulphurisation tests, the COS content of outlet gases becomes 245 ppm, in other words an increase in COS content is observed and a similar decrease in H$_2$S content is detected. This fact can be explained by reaction (9) due to increasing CO content as a result of the reverse water-shift reaction (7).

When dolomite is used under the same gas composition conditions, Fig. 14 (tests 3, 12 and 16), the COS and H$_2$S breakthrough curves have the same shape and are virtually identical, regardless of whether the curve is more or less "perfect". (To be able to compare both, the maximum amount produced by both composites is normalised to 100%). The same occurs with the curve obtained with another different composition of sulphurant gas without added water (test 16) (● and ○).

This suggests that H$_2$S and COS are linked by one or more chemical equilibria and that there may be competition between reactions (3), (5), and (9). However, given the direct relationship of curve shape and the H$_2$S content with COS in each specific case of each curve, it seems that reactions (5) and (9) are the two that basically control the appearance of COS (the amount of CO$_2$ and H$_2$ present is much higher than the COS generated in all cases, except when neither CO$_2$ nor H$_2$O is used).

Under test conditions, the presence of CS$_2$ has not been detected in the outlet gases and, therefore, reaction (6) does not occur.

![Fig. 13. COS in the outlet gas (11.4 cm). COS breakthrough curves with the usual inlet gas composition (2% H$_2$S, 6% CO$_2$, 10% H$_2$O) for tests (Table 1) 3 (■), 12 (●) and 18 (○). Without CO$_2$, test 16 (○). Without CO$_2$ and H$_2$O, test 7 (●). Lower horizontal solid line: COS introduced.](image)

![Fig. 14. H$_2$S and COS breakthrough curves under different operating conditions for tests (Table 2) 3 (■, ○), 12 (●, A) and 16 (●, ○). (H$_2$S: ■, ●, and COS: ○, A).](image)

<table>
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<tr>
<th>Test</th>
<th>Ca converted to CaS%</th>
<th>Test conditions</th>
<th>Inlet gas (N$_2$ balance gas)</th>
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<tr>
<td></td>
<td>(%)</td>
<td>Bed height (cm)</td>
<td>Gas velocity (cm s$^{-1}$)</td>
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<td>10</td>
<td>39</td>
<td>11.4</td>
<td>29.1</td>
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</table>
3.3. Influence on reverse water-shift reaction

At the beginning of the sulphidisation process, when practically all \( \text{H}_2\text{S} \) reacts with \( \text{CaO} \) generated during dolomite calcination, an additional 2% of water is produced as in reaction (1) and this alters the equilibrium of reaction (7).

A variation in \( \text{CO}_2 \) is observed from start to finish of the sulphidisation process, in which practically no water is produced and in which only water introduced in the gaseous mixture takes part. Fig. 15 (test 12) shows that, in comparison with silica, the reaction rate is highly accelerated; the \( \text{CO}_2 \) level reached when dolomite is switched to silica is shown (solid line at the top of the plot).

The mean value calculated for the equilibrium constant of reaction (7) (eliminating the two initial points which are clearly outliers) is 1.14, a figure consistent with the theoretical value of this constant at 850 °C (1.144). The same occurs when operating at 900 °C or 950 °C.

Fig. 15 also shows the \( \text{CO}_2 \) emission curves as absolute values of a series of tests carried out under different conditions (gas composition, gas velocity) (tests 3, 10 and 13) but with the same gas composition (2% \( \text{H}_2\text{S} \), 18% \( \text{H}_2 \), 6% \( \text{CO}_2 \) and 10% \( \text{H}_2\text{O} \)). Two lines have also been marked: one at 176 ppm corresponding to the amount introduced in the case of tests with 2% \( \text{H}_2\text{S} \) and another at 245 ppm corresponding to the amount present when the same gas is passed through silica at 850 °C (test 20, Table 2), which corresponds to the conditions of most tests carried out.

The curve corresponding to test 10 carried out under the same conditions as with silica gives a maximum \( \text{CO}_2 \) value (●) only slightly below that corresponding to silica, which demonstrates similar behaviour when dolomite is saturated or completely sulphurised. The curve corresponding to test 13 (●), carried out at a slower gas velocity and higher temperature (900 °C) shows a similar trend, although its peak value is slightly below the previous case. This also occurs with the curve from test 3 (●). In all cases, the value is higher than the initial \( \text{CO}_2 \) content. This demonstrates the low influence of grain size, gas velocity and temperature (in the range of 850-900 °C tested) on maximum \( \text{CO}_2 \) if the gas composition is the same. This can be related to the equilibrium of chemical reaction (9) described above.

The influence of gas composition is evident in the curve from test 7 (●), carried out without added \( \text{CO}_2 \) or \( \text{H}_2\text{O} \). This curve has been discussed above and shows emissions of about 1.5 ppm of \( \text{CO}_2 \). The behaviour is the same as for silica under the same conditions. This is easily explained by the equilibrium between \( \text{H}_2\text{S} \) and \( \text{CO}_2 \): if there is no \( \text{CO} \) except for the minimum amount produced by reaction (9), then this reaction is nearly completely shifted toward the right, causing the decomposition of \( \text{CO}_2 \).

In contrast with the above paragraph, test 16 (Table 2) done without added steam shows that higher values of \( \text{CO}_2 \) were obtained. The main difference from the test is the non-addition of water: only water generated in reactions (1) and (7) is present. This curve is identical to that of \( \text{H}_2\text{S} \) (Fig. 13); however, because there is a higher absolute value than with the most frequent gas composition used, hydrolysis reaction (3) is reduced due to the lower presence of \( \text{H}_2\text{O} \) and the higher level of \( \text{CO} \) shifts reaction (9) toward the left contributing to this higher \( \text{CO}_2 \) result.

4. Conclusions

(1) The principal factors for the decrease in \( \text{H}_2\text{S} \) content in the outlet gases are bed material and temperature. Lower gas velocities, higher \( \text{H}_2\text{S} \) concentrations and higher bed lengths result in lower \( \text{H}_2\text{S} \) content in outlet gases.

(2) Dolomite position at the top of the desulphurant bed or bottom (under more static pressure) is another important factor that conditions its use. The behaviour at the bottom is worse with smaller grain sizes.

(3) A temperature between 850 °C and 950 °C has very little influence on the overall characteristics of the breakthrough curves and only a slight influence on the initiation of the curves due to the influence of temperature on the equilibrium constant.

(4) Lower steam and \( \text{CO}_2 \) concentrations in the inlet gas lead to significant reductions in the amount of \( \text{H}_2\text{S} \) present in the outlet gas in the initial adsorption stage of \( \text{H}_2\text{S} \).

(5) To reach an upper threshold (e.g., 400 ppm) of \( \text{H}_2\text{S} \) at the outlet, dolomite conversion with a bed length of 17 cm is approximately 68% with 2% \( \text{H}_2\text{S} \), 6% \( \text{CO}_2 \), 18% \( \text{H}_2 \) and 10% steam in the inlet and approximately 2.6% \( \text{CO}_2 \), 14.6% \( \text{H}_2 \) and 15.4% water at the outlet.

(6) Any \( \text{CO}_2 \) present shows the same trend as \( \text{H}_2\text{S} \) in its breakthrough curves.

(7) Temperature (850 °C or 900 °C) has very little influence on the resulting \( \text{CO}_2 \).

(8) The amount of \( \text{CO}_2 \) present in the outlet gases is highly dependent on the composition of the gas, especially the content of \( \text{H}_2\text{S} \), \( \text{H}_2 \), \( \text{CO} \) and steam.

(9) Sulphidised dolomite acts as a catalyst for the reverse water-shift reaction, enhancing equilibrium at the temperature indicated. This should be considered when the intention is to produce hydrogen in the presence of \( \text{CO}_2 \).

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Reference


