Effect of Fuel Gas Composition in Chemical-Looping Combustion with Ni-Based Oxygen Carriers. Part 1. Fate of Sulfur.

*Francisco García-Labiano, Luis F. de Diego, Pilar Gayán., Juan Adánez, Alberto Abad and Cristina
Dueso*

Department of Energy and Environment, Instituto de Carboquímica (C.S.I.C.)

Miguel Luesma Castán 4, 50018 Zaragoza, Spain

E-mail: glabiano@icb.csic.es

**RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required
according to the journal that you are submitting your paper to)**

* Corresponding Author. Tel.: +34-976-733977; fax: +34-976-733318; *E-mail address:*
glabiano@icb.csic.es (F. García-Labiano)

ABSTRACT.

Chemical-Looping Combustion (CLC) has been suggested among the best alternatives to reduce the economic cost of CO₂ capture using fuel gas because CO₂ is inherently separated in the process. As gaseous fuels it can be used natural gas, refinery gas or syngas from coal gasification, which may

contain different amounts of sulfur compounds, such as H_2S and COS . An experimental investigation of the fate of sulfur during CH_4 combustion in a 500 W_{th} CLC prototype using a Ni-based oxygen carrier has been carried out. The effect on the oxygen carrier behavior and combustion efficiency of several operating conditions such as temperature and H_2S concentration has been analyzed. Nickel sulfide, Ni_3S_2 , was formed at all operating conditions in the fuel reactor, which produced an oxygen carrier deactivation and lower combustion efficiencies. However, the oxygen carrier recovered their initial reactivity after certain time without sulfur addition. The sulfides were transported to the air reactor where SO_2 was produced as final gas product. Agglomeration problems derived from the sulfides formation were never detected during continuous operation. Considering both operational and environmental aspect, fuels with sulfur contents below 100 vppm H_2S seems to be adequate to be used in an industrial CLC plant.

1. Introduction

The carbon dioxide concentration in the atmosphere has increased strongly over the few past decades, being the combustion of fossil fuels for power generation one of the main sources of carbon dioxide emissions. The relation between CO_2 concentration and global warming is clear and it is generally accepted that reduction in greenhouse gas emissions is necessary as soon as possible to avoid major climate changes. Up to now, the interest to achieve the reduction of CO_2 has been focused on improving energy efficiency, the use of renewable sources (biofuel, wind power, etc.) and the change to fuels with lower carbon content. However, these solutions will not probably allow reaching the desired low levels of CO_2 emissions. CO_2 capture and sequestration (CCS) would be an additional option to reduce CO_2 concentration in the atmosphere.¹ There are different CCS technologies available or currently under development but most of them have high energy penalty as a consequence of a CO_2 separation step, which result in an increase of the energetic and economical cost.

Chemical-Looping Combustion (CLC) process has been suggested among the best alternatives to reduce the economic cost of CO_2 capture using fuel gas because CO_2 is inherently separated in the

process from the other flue gas components (N_2 and unused O_2) and thus no energy is expended for the separation.² In CLC, oxygen is transferred from the air to the fuel by means of an oxygen carrier (OC) in the form of a metallic oxide, thus avoiding the direct contact between the combustion air and the fuel. The solid circulates between two interconnected reactors, the fuel (FR) and the air reactor (AR). In the FR, the metal oxide reacts with the gaseous fuel to produce CO_2 and H_2O . Pure CO_2 , ready to compression and sequestration, will be readily recovered by condensing the steam. The OC is oxidized again in the AR, and it is ready to start a new cycle. The heat involved in the global process is the same as for normal fuel gas combustion. This process also ensures that no NO_x will be present in the flue gas as a result of the introduction of fuel and air into different reactors and of the moderate AR operating temperature.

As gaseous fuels in the CLC process can be used natural gas, refinery gas or synthesis gas from coal gasification. The CLC process has been demonstrated for natural gas in plants at scales of $10 \text{ kW}_{\text{th}}$ ³⁻⁶, $50 \text{ kW}_{\text{th}}$ ⁷, and $120 \text{ kW}_{\text{th}}$ ⁸. The use of syngas has been analyzed at lower scales, $\approx 300\text{-}500 \text{ W}_{\text{th}}$.⁹⁻¹² However, the real fuel gases may contain different amounts of light hydrocarbons (LHC) and sulfur compounds, such as H_2S and COS . The effect of the presence of LHC is investigated in the second part of this work.¹³ The natural gas usually contains very small amounts of H_2S ($\approx 20 \text{ vppm}$).¹⁴ H_2S content in refinery fuel gas can vary depending on the site but contents up to 800 vppm can be found, and this value can be increased up to 8000 vppm for raw syngas.¹⁵

The design of an industrial CLC plant can be affected by the presence of these sulfur compounds in a double way. From the environmental point of view, the sulfur fed into the system can be released as SO_2 in the AR gas outlet stream and must fulfill the legislation about emissions. Moreover, the presence of sulfur compounds on the FR gas stream may be made necessary the installation of a desulphurization unit to fulfill the requirements needed for the compression, transport and storage of the CO_2 produced in the plant.^{16,17} From the operational point of view, the reaction of these sulfur compounds with the OC may form several sulfur compounds that probably are poisonous to OC, decreasing their reactivity and

therefore, the combustion efficiency of the process. This process is especially important when Ni-based oxygen carriers are used.¹⁸⁻²⁰ Moreover, the low melting point of some sulfides could produce agglomeration and affect to the solids circulation pattern between the interconnected FB reactors.²¹ Depending on the intensity of the above processes, it could be necessary to desulfurize the fuel previously to their use in the CLC process.

Up to now, only thermodynamic studies can be found in the literature about the effect of sulfur in a CLC process. Mattisson et al.²¹ carried out a thermodynamic study about the fate of H₂S in a CLC system using NiO as oxygen carrier and methane as fuel. They obtained that H₂S may be oxidized to SO₂ in the FR by oxidants such as H₂O, CO₂ and even the NiO. The degree of conversion to SO₂ is enhanced at high temperatures and low pressures. Both SO₂ and H₂S could react with the oxygen carrier (NiO or Ni) to form sulfides or sulfates (NiS, NiS₂, Ni₃S₂ or NiSO₄). They calculated that NiSO₄ will not be formed at the conditions which may be encountered in the FR, and that Ni₃S₂ was the thermodynamically most stable sulfide. The main difficulty of sulfides formation takes root in their low melting point that could lead to the OC agglomeration and produce operational problems in the system.

Later works extended the calculations to other OC and fuel gas although they reached similar conclusions with respect to the use of NiO as oxygen carrier. Jerndal et al.²² investigated the thermodynamics of several OC based on Ni, Cu, Fe, Mn, Co, W and sulfates of Ba and Sr with regard to the carbon deposition and formation of sulfides and sulfates and using CH₄, CO and H₂ as gas fuels. Wang et al.²³ carried out a thermodynamic investigation about carbon deposition and sulfur evolution in CLC with syngas, when using NiO, CuO, Fe₂O₃, Mn₃O₄, and CoO.

Up to now, no experimental works related with the presence of H₂S in the fuel gas of a CLC process can be found in the literature. It must be remarked that the thermodynamic analysis considers the final condition at equilibrium but does not consider intermediate conditions due to kinetic constraints, concentration variations happening at different locations of a fluidized bed or temperature gradients occurring in a real process.

The aim of this work was to test by the first time the behavior of a Nickel-based oxygen carrier when the fuel, CH₄, contains variable amounts of H₂S under continuous operation in a 500 W_{th} CLC pilot plant. The influence of temperature and H₂S concentration on gas products distribution and combustion efficiency, oxygen carrier deactivation, sulfur splitting between FR and AR, and material agglomeration was investigated.

2. Experimental

2.1. Oxygen carrier

The oxygen carrier used in this work was prepared by hot incipient wet impregnation (HIWI) using NiO as active phase and α -Al₂O₃ as support. Previous works were carried out to determine the effect of the support on the Ni-based OC.²⁴ Commercial γ -Al₂O₃ (Puralox Nwa-155, Sasol Germany GmbH) particles of 100-300 μ m were sintered in a furnace at 1423 K for two hours to obtain α -Al₂O₃ as support (ρ = 1900 kg/m³, ε = 48.5 %). The material was prepared by the addition over the hot α -Al₂O₃ (353 K) of a volume of a saturated solution (6 M) of Ni(NO₃)₂·6H₂O (>99.5% Panreac) at 333-353 K, which corresponds to the total pore volume of the support particles. The aqueous solution was slowly added to the support particles with thorough stirring at 353 K in a planetary mixer. The desired active phase loading was achieved by applying two successive impregnations followed by calcinations at 823 K, in air atmosphere for 30 minutes, to decompose the impregnated metal nitrate into insoluble oxide. Finally, the OC was calcined for 2 hours at 1223 K, obtaining a material –denoted here as Ni19- α Al:HI– whose main characteristics are showed in Table 1. The oxygen transport capacity was defined as the mass fraction of oxygen that can be used in the oxygen transfer, calculated as $R_{OC} = (m_{ox} - m_{red})/m_{ox}$, where m_{ox} and m_{red} are the masses of the oxidized and reduced form of the oxygen carrier, respectively.

2.2. CLC prototype (500 W_{th})

The schematic diagram of the 500 W_{th} Chemical-Looping Combustion prototype used for the experimental tests is shown in Figure 1. The total solid inventory in the system was about 1.3 kg of oxygen carrier.

The FR consisted in a bubbling fluidized bed (0.05 m i.d.) with a bed high of 0.1 m. In this reactor, the CH_4 reacts with the oxygen carrier to give CO_2 and H_2O . The solids reduced in the FR were then transported to the AR through a nitrogen-flowing loop seal to prevent mixing of the fuel gas in FR and the oxygen in AR while solids were flowing through it. The AR was a bubbling fluidized bed (0.05 m i.d.) whose bed height was 0.1 m, followed by a riser of 0.02 m i.d. and 1 m height. The fully oxidized carrier was recovered by a high-efficiency cyclone, and sent to a solid reservoir, ready to start a new cycle. A solid valve situated below the cyclone allowed the measurements of the solid flow rates. Fine particles formed by attrition/fragmentation during operation were recovered both in the cyclones and filters located in the FR and AR lines.

The prototype had several tools of measurement and system control. Thermocouples and pressure drop transducers located at different points of the plant showed the current operating conditions at any time. Specific mass flow controllers gave accurate flow rates of feeding gases. The gaseous outlet streams of the FR and AR were drawn to respective on-line gas analyzers to get continuous data of the gas composition. CH_4 , CO , H_2 , and CO_2 concentrations in the gas outlet stream from the FR were measured after steam condensation. O_2 , CO , and CO_2 concentrations were obtained at the gas outlet stream from the AR. CH_4 , CO and CO_2 concentrations were measured by non-dispersive infrared (NDIR) analyzers (Maihak S710 / UNOR), O_2 concentration was determined using a paramagnetic analyzer (Maihak S710 / OXOR-P), and H_2 concentration by a thermal conductivity detector (Maihak S710 / THERMOR). All data were collected by means of a data logger connected to a computer.

To study the effect of sulfur on the oxygen carrier, the CLC pilot plant was modified by including two mass flow controllers for H_2S and H_2 . H_2 , in small amount, was used to avoid the decomposition of H_2S in the feeding lines. Some specific analyzers for sulfur compounds were used for the outlet streams of the fuel and air reactors. A non-dispersive infrared (NDIR) analyzer (Siemens Ultramat U22) was used to detect the SO_2 concentrations obtained at the AR gas outlet stream. For the gas analysis of the FR, NDIR analyzers showed problems of cross-interference between gases. Thus, a gas chromatograph

(Varian 3400-CX GC) equipped with a PORAPAK-Q packed column for chromatographic separation and a sulfur-specific flame photometric detector (FPD) was used. In this way, it was possible the detection of the different gaseous sulfur compounds that can be appeared in the FR as H_2S , SO_2 , COS , CS_2 , etc. The chromatograph was calibrated in the range 0-200 vppm for H_2S and SO_2 .

Moreover, the prototype allowed the collection of solid material samples from the AR and riser line at any moment from the diverting solid valve, and from the FR at the end of the test.

3. Results

3.1. Thermodynamic calculations

Potential fuels for a CLC process, such as natural gas, refinery gas or syngas, may contain variable amounts of sulfur compounds like H_2S . This undesirable gas could be partially oxidized in the FR by oxidants such as H_2O , CO_2 or the metal oxide and different solid and gaseous species may be present (sulfides, sulfates, S_2 , SO_2 , COS). Several works have made thermodynamic calculations about the fate of H_2S in a CLC process depending on the metal oxide selected as oxygen carrier, the operating conditions (temperature, pressure, and H_2S concentration), and the fuel gas (CH_4 , CO or H_2).²¹⁻²³

To select the operating conditions to be used in the CLC prototype, several thermodynamic calculations were carried out using the HSC Chemistry 6.1 software.²⁵ The program finds the most stable phase combination and seeks the phase composition where the Gibbs energy of the system reaches its minimum at a fixed mass balance, constant pressure and temperature. The calculations about the fate of sulfur were related with the use of Ni-based oxygen carriers in a CLC process working at atmospheric pressure and using CH_4 as fuel.

The first thermodynamic study was the calculation of the equilibrium concentrations at 1143 K of the sulfur-containing species in a typical atmosphere present in the FR as a function of H_2S content in the fuel gas (see Figure 2). The values were expressed as the percentage of sulfur present in the gas products in relation to the sulfur fed into the system. At H_2S concentrations below 500 vppm, most of the H_2S introduced into the system is used to form SO_2 . However, at higher concentrations, the

formation of Ni_3S_2 increases. As previously mentioned, Ni_3S_2 is the most stable sulfide at the typical temperatures of CLC process.

To analyze the effect of temperature on the sulfides formation process, another thermodynamic calculation was made for a fixed H_2S concentration of 300 vppm (see Figure 3). For this concentration, Ni_3S_2 appears only at temperatures below 1113 K. At higher temperatures, most of the H_2S fed is oxidized to SO_2 . Lower H_2S concentrations in the initial feeding shift the zone of no sulfides formation to lower temperatures, and higher H_2S concentrations shift the plots towards the right.

If Ni_3S_2 is produced in the FR, this can be transferred to the AR coupled to the oxygen carrier. In the oxidant atmosphere of the AR, the sulfide can be oxidized to NiSO_4 or be converted into NiO and SO_2 , depending on temperature, and O_2 and SO_2 concentrations. Figure 4 shows the decomposition curve of the NiSO_4 as a function of the SO_2 partial pressure and temperature for three different O_2 concentrations. At temperatures above 873-923 K, the NiSO_4 can decompose into NiO and SO_2 even in atmospheres highly concentrated in SO_2 . The oxygen concentration has a small effect on the NiSO_4 decomposition temperature.

3.2. Experimental tests with H_2S addition

To determine the effect of H_2S on the behavior of the Ni-based oxygen carrier, several tests were carried out in the CLC prototype under continuous operation. As above mentioned the H_2S present in the gas fuel can be turned into several gaseous or solid compounds depending on the operating conditions in the CLC system. The experiments herein carried out were designed based on the previous thermodynamic calculations. The purpose was to know the effect of H_2S feeding on the reactivity and agglomeration behavior of the OC as well as on the sulfur splitting between the reactors. It is well known the poisoning effect of the H_2S on the Ni sites and the subsequent loss of reactivity.¹⁸⁻²⁰ It must be also considered that the sulfides formation may present operational difficulties as a consequence of the low melting point of these compounds, i.e 1062 K for the Ni_3S_2 .

Table 2 shows the operating conditions selected to avoid (tests 1, 2, 3 and 4) or to favor (tests 5, 6 and 7) the formation of nickel sulfide during continuous operation in the prototype, according to thermodynamic considerations. Every test corresponds to one day of operation, and about five hours of continuous operation with H₂S feeding. During tests 6 and 7, the H₂S concentration was increased after 4 hours of steady state operating conditions to analyze the performance of the OC with a higher H₂S concentration. Test 0 corresponds to the reference conditions without H₂S feeding, and in test 1 the H₂S was fed after two hours of operation at reference conditions.

During test 0, CH₄ (30 vol%) was used as fuel gas, and the temperatures in the FR and AR were set at 1143 and 1223 K, respectively. At these conditions, the gas velocities at the inlet of the FR were 0.1 m/s and 0.45 m/s at the inlet of the AR. The solids circulation rate was fixed at 14 kg/h. It must be remarked that the methane conversion was complete, and the CO and H₂ concentrations (≈ 0.3 and ≈ 1.3 , respectively) were close to the theoretical values given by the thermodynamic equilibrium. CO₂ concentration was $\approx 24\%$ as a consequence of the dilution produced by the N₂ coming from the loop seal. Neither CO₂ nor CO was detected in the AR gas stream, which indicated the absence of gas leakage between reactors and no carbon formation in the FR. The operation of the plant was very stable for a long time, ≈ 6 hours, so this can be considered as a good reference value of the steady state operation.

Figure 5 shows the dry basis concentrations obtained at the outlet of the FR and AR for test 1. The first 2 hours corresponds to the reference operating conditions used in test 0, and after that, 500 vppm of H₂S was fed into the system. After H₂S feeding, CO₂ decreased and some unconverted CH₄ appeared ≈ 10 minutes later, while the CO and H₂ concentrations increased slowly up to 1.5 and 3, respectively. These effects were attributed to an OC deactivation by the presence of sulfides, which prevents the catalytic action of the metallic Ni on the partial oxidation and CH₄ reforming. H₂S and SO₂ were found at very low concentrations (< 10 vppm) in the FR outlet stream. Moreover, SO₂ was detected in the AR and their concentration increased with time, which indicated the transfer of sulfur as nickel sulfide from

the FR to the AR through the oxygen carrier. These results indicated that a part of the sulfur fed into the FR was released as SO_2 in the AR and the other was being accumulating in the OC as sulfides or sulfates. These results did not follow the expected pattern according to the previous thermodynamic study.

As an example of the experimental data obtained during longer tests with H_2S addition, Figure 6 shows the temperature and gas product distribution profiles obtained in FR and AR during test 3. The operating conditions of this test correspond to the zone where the nickel sulfides formation should not be produced, according to the thermodynamic calculations showed in Figure 3. The solids used in test 2 were heated in air and started solids circulation. The CH_4 feeding started after reaching the desired temperatures in the reactors. At the beginning, some CH_4 was detected at the outlet of the FR due to the presence of sulfides or sulfates in the OC formed in the previous test. However, the CH_4 concentration was decreasing and the CO_2 increasing until reach steady state conditions similar to the reference test. Some SO_2 was detected as a consequence of the solid sulfur compounds decomposition. These facts indicated that the OC was able to recover their reactivity after certain time without H_2S feeding as will be deeply explained later. After H_2S feeding started the deactivation of the OC with similar consequences to the above explained in Figure 5.

A similar behavior, although quantitatively different, was observed in all the tests carried out with H_2S feeding. For a better comparison, Figure 7 shows the CO_2 concentration obtained for all tests after H_2S feeding. This concentration gives an indication of the variation with time of the OC reactivity at different operation conditions. It is evident from the Figure that the loss of reactivity is more important as highest is the H_2S concentration fed and lower is the temperature, tests 6 and 7, where the formation of sulfides was thermodynamically favored. However, it should be highlighted the low effect of H_2S feeding when small amounts of H_2S were introduced, i.e., the test 4 with 100 vppm.

The behavior of the OC was qualitatively similar in all the tests, so it was concluded that sulfides were produced under all the operating conditions. The low amount of sulfur in the solid samples made

impossible the detection of Ni_3S_2 by X Ray Diffraction (XRD) analysis, although this sulfide is the most stable compound at the typical temperatures of CLC. As commented before, SO_2 was detected at the AR outlet stream and its concentration depended on the H_2S concentration fed into the FR. The sulfides formed in the FR can react in the oxidant atmosphere of the AR to give SO_2 , which depends on the temperature and O_2 concentration.

To analyze the effect of temperature on the SO_2 removal, the AR temperature was varied during tests 5 and 6. It was found that the SO_2 concentration measured at the outlet of AR and riser was zero at temperatures below 1193 K, and exhibited a quick increase when the temperature was set at 1223 K. At temperature below 1193 K, there was an accumulation of sulfur in the OC and their reactivity continued decreasing slowly. To know the accumulation of sulfur, Figure 8 shows the SO_2 concentration after 5 hours of continuous operation as a function of the H_2S concentration compared to the theoretical value obtained if all the sulfur fed into the system would be released as SO_2 in the AR. It can be observed that sulfur was accumulated in the OC at all operating conditions. It must be considered, however, that due to the specific characteristics of the prototype, the temperature in the top of the riser is about 1073 K during operation. In this case, the SO_2 release in the AR could react with the NiO in the oxidant atmosphere of the riser to form again NiSO_4 .

In any case, the formation of sulfides in the FR was evident from the experimental data even in those operating conditions selected to avoid sulfides formation (see Table 2). To explain this phenomenon, new thermodynamic calculations were carried out to simulate the gas atmosphere in the lower zone of the FR, which is a bubbling fluidized bed. In this area, an excess with regard to NiO of methane or their incomplete combustion products, CO and H_2 , was present. Figure 9 shows the distribution of sulfur-containing products as a function of CO and H_2 concentration in the gas stream. It is observed that for CO + H_2 concentrations above 0.4%, the formation of nickel sulfide is very important at 1143 K. This situation would be also valid for the upper part of the fluidized bed reactor if the fuel is not fully converted, where the CO and H_2 concentrations are over the values given by the thermodynamic

equilibrium. Based on these results it can be concluded that the formation of sulfides would be possible in the CLC system at all the operating conditions showed in Table 2.

3.3. Regeneration of the oxygen carrier

As above showed, it is clear that H_2S and SO_2 react with the NiO or Ni present in the OC at typical conditions of temperature and pressure present in a CLC system. The formation of sulfides and sulfates produces the OC deactivation and, therefore, lower combustion efficiency. An important question to solve was to know if the process of reactivity loss was definitive or reversible.

Figure 10 shows the variation of CO_2 (dry basis) through the whole time of experimental work carried out with the same OC. The decrease in CO_2 concentration was associated with a loss of reactivity due to sulfides/sulfates formation, and the CO_2 increase corresponds to the regeneration stage. It was found that the OC recovered its combustion capacity after a combustion period of 1-2 hours without H_2S addition, (see first part of Figure 6). The regeneration was almost complete in all cases, even in the experiments where a high amount of sulfides and/or sulfates had been produced in the previous test.

To know the variation of the OC reactivity with tests, some samples were taken from the system after every regeneration step. The reactivity of these samples was carried out in a thermogravimetric analyzer (TGA) using CH_4 during the reduction and air for the oxidation at 1223 K using the methodology described in previous works.²⁶ Figure 11 shows the conversion versus time data for the different samples, which were compared with data corresponding to the fresh OC. The data corresponds to the third cycle of reduction-oxidation in the TGA. The reactivity was very high in all cases with almost complete conversion before a minute in both the reduction and the oxidation. These results corroborate that the OC recovered their initial reactivity after some time without H_2S feeding.

3.4. Fate of sulfur on oxygen carrier agglomeration

Previously to the experiments showed in this work, there were several doubts about the fact of the sulfur, not only on the OC reactivity loss but also on the possible agglomeration of the solids, which could affect the FB behavior and the solids circulation pattern in the whole system.²¹ This was as

consequence of the low melting point (1062 K) of the Ni_3S_2 , the thermodynamically most stable sulfide at high temperatures. However, no experimental evidence of this phenomenon was previously obtained.

During the whole experimental time herein carried out, which corresponds to a total of 35 hours with H_2S addition, the solid circulation rate was maintained almost constant, ≈ 14 kg/h, and never were detected agglomeration problems in the system. It can be concluded therefore that agglomeration should not be a problem for a typical CLC process operating with this type of oxygen carriers.

3.5. Sulfur splitting

As it has been previously shown, sulfur fed with the fuel to the FR is distributed between the gaseous sulfur species obtained at the outlet gases from FR and AR, and the solid sulfur species formed on the OC. The sulfur splitting among the above options depended on the operating conditions existing on the system. The emission of H_2S and SO_2 from the FR were very low, < 10 vppm, in all the experimental tests. SO_2 emitted at the AR outlet stream was directly related with the H_2S concentration fed into the FR, and if temperature in AR was higher than 1203 K. The rest of the sulfur remained in the solid as sulfides or sulfates.

Sulfur mass balances were carried out by integration of the sulfur compound concentration present at the AR and FR outlet streams and in the OC particles, determined by proximate analysis of samples taken after 5 hours of continuous CLC operation. However, high uncertainty was obtained in the data values due to the low sulfur content of the samples. Assuming steady state and considering data after 5 hours of continuous operation, sulfur balances in Table 3 indicates the gradual accumulation of sulfur in the OC particles.

4. Discussion

4.1 Reactions involving Sulfur in a CLC system

A compilation of all the possible reactions involving sulfur at typical CLC operating conditions was made both in the fuel and air reactor. Using CH_4 as fuel and NiO as oxygen carrier, the overall reaction in the FR is

When Ni is present, CO and H₂ can appear by lateral reactions as partial oxidation and methane reforming, and later react with the NiO,

If the fuel gas contains sulfur compounds, the number of reactions that can appear in the FR increase. The main component in fuel gases, H₂S, can react with any of the solid materials to form nickel sulfides. Thermodynamic calculations showed that Ni₃S₂ was the most stable sulfide at high temperatures typical of CLC, compared to NiS and NiS₂.^{21, 23}

The sulfides can be also reduced by the fuel gases (CO, H₂), or react with the gaseous final products (CO₂, H₂O). Reactions 7 and 9 are the reverse reactions of reactions 4 and 5.

In the gas phase, the H₂S may be oxidized to SO₂ by oxidants such as H₂O or CO₂,

Moreover, in a system with solids circulation some nickel sulfate may be fed to the FR coming from the AR. The sulfates can be reduced by the fuel gases or decompose at high temperature to release SO₂.

With respect to the AR, the metallic nickel is oxidized with the oxygen

The nickel sulfides coming from the FR can react with the oxygen present in the AR to give sulfates or NiO and SO₂ depending on the AR temperature and O₂ and SO₂ concentrations.

In gas phase, SO₃ can be formed by oxidation of SO₂

4.2. Reactions involving sulfur in the 500 W_{th} CLC prototype.

According to the results obtained in this work, information about the reactions produced in our 500 W_{th} CLC prototype with presence of sulfur was obtained. It is clear that nickel sulfides were formed in the FR by reactions 4 and 5, considering that Ni₃S₂ is the most stable compound at high temperatures. The small amounts of H₂S and SO₂ and other sulfur compounds detected at the outlet of the FR would be the corresponding to the combination of all the possible reactions 1-15 taking place in this reactor. The Ni₃S₂ is transferred to the AR on the oxygen carrier. In an oxidative atmosphere, nickel sulfide could be transformed, depending on the AR temperature, into nickel sulfate (reaction 17) or into NiO and SO₂ by two ways: directly (reaction 19) or through the sulfate decomposition (reactions 17 and 18). According to thermodynamic, NiSO₄ should decompose at temperatures above 923 K, even at high O₂ concentrations (see Figure 4). Therefore, it is possible that the SO₂ released in the AR at temperatures higher than 1203 K could react again with the NiO and O₂ to give NiSO₄ in the riser, which was at lower temperatures. Another possibility is that kinetic restrictions limit the sulfate formation in the AR. In any case, the continuous accumulation of sulfur in the OC means that some solid sulfur compound was recirculated into the FR. The majority of them will be as sulfates although depending on the

operating conditions the solid recirculated could also contain some sulfide without react. The NiSO_4 recirculated will react in the reducing atmosphere of the FR to again produce sulfides (reactions 12-14). The nickel sulfide-sulfate pair would act as an oxygen carrier between the FR and the AR, although the detrimental aspect of the sulfur presence does not compensate the possible advantages of a possible oxygen transport.

4.3. Implications of sulfur in an industrial CLC plant.

The design of industrial CLC plants must consider both operational and environmental aspects regarding sulfur content of fuel gas.

From the operational point of view, the reaction of the sulfur compounds with the OC may form several sulfides and sulfates that are poisonous to the OC, decreasing their reactivity and therefore, the combustion efficiency of the process. Moreover, the low melting point of some sulfides could produce agglomeration and affect to the solids circulation pattern between the interconnected FB reactors. According with the experimental work herein carried out, the OC deactivation was of low magnitude for H_2S concentrations of 100 vppm. Moreover, if the temperature in the AR and riser is high enough, the sulfur fed into the FR can be released as SO_2 and the OC will be returned to the FR fully reactivated. It must be also considered that during the tests carried out at the 500 W_{th} prototype, no operational problems were found as a consequence of the sulfides/sulfates formation.

From the environmental point of view, by one hand, the SO_2 emissions released from the AR must fulfill the legislation about emissions. The very restrictive legislation about sulfur emissions for gaseous fuels (35 mg/Nm^3 or ≈ 12 vppm is currently applicable for $>50 \text{ MW}_{\text{th}}$) limit the maximum sulfur content in the fuel gases to ≈ 120 vppm H_2S , considering that all the sulfur fed is released as SO_2 in the AR. It must be considered that for CH_4 as fuel gas, the dilution produced in the AR is about 10 times as a consequence of the air/fuel molar ratio and the high presence of inert N_2 in air.

On the other hand, a part of the sulfur can be also released in the FR gas stream. From the experiments herein carried out, very low concentrations of H_2S and SO_2 were obtained in this stream, with typical

values < 10 vppm, even in those cases with very high sulfur contents in the fed (up to 1000 vppm H_2S). It is known that flue gas impurities, such as SO_x , NO_x , etc. have the potential of interacting unfavorably with compression, and pipeline transport of CO_2 , as well as on storage. With respect to compression, the existence of gas mixtures can produce condensation of the higher boiling constituents, which may limit the ability to achieve adequate interstage cooling and may damage the compressor and other related equipment. Moreover, materials used in separation, compression, and transmission are subjected to corrosion by sulfuric or sulfurous acids.¹⁶ However, there is not a clear idea about the allowed limit of sulfur compounds and their effect on the cost during compression and transport of the CO_2 . The presences of sulfur impurities can be also have effects on the storage of the CO_2 obtained in the CLC process.¹⁷ The treatment of the flue gas downstream the FR will depend on the purity requirements of the liquefied CO_2 . Currently, there is no legislation about contaminant contents in CO_2 for storage, and much uncertainty exists about these limits. In the literature, very different values can be found ranging from $<200 \text{ mg/Nm}^3$ for a modest CO_2 quality to $<5 \text{ mg/Nm}^3$ for a very high CO_2 quality.²⁷

According to the above considerations and the experimental data obtained in the tests carried out in the 500 W_{th} CLC prototype, several options can be adopted in an industrial CLC plant regarding sulfur in fuel.

The use of high sulfur content fuels in a CLC process can be problematic. Although no operational problems derived from agglomeration are expected, the OC deactivation will produce an important decrease in combustion efficiency. Moreover, the composition of the flue gas obtained at the outlet, both from the AR and the FR, will force to include new downstream units to overcome both technical and legal restrictions.

Therefore, the more realistic option would be to avoid the sulfur components entering the CLC system. Processes to remove sulfur components from fuel gas streams are widely applied in industry, including solvent treatment with amines, ZnO adsorbents, etc.²⁸ The key aspect would be the maximum sulfur content to be allowed by a fuel to be used in a CLC process. The limit would be ≈ 100 ppm of H_2S

considering the low deactivation effect on the OC observed during the tests herein carried out, and that will fulfill legislation about emissions if all SO_2 is released as SO_2 in the AR. Moreover, no operational problems derived from solids agglomeration would be expected. In current refinery practice the gaseous fuel sulfur concentration is designed below 20 vppm. Therefore, these gases could be an adequate fuel to be used in a CLC plant.

4. Conclusions

Several tests have been carried out in a CLC prototype (500 W_{th}) under continuous operation with a Ni-based oxygen carrier to analyze the effect of sulfur content of fuel in relation to CH_4 combustion efficiency, oxygen carrier reactivity and agglomeration process. The tests were programmed at operating conditions where the formation of sulfides was favored or not.

The presence of H_2S produced always a decrease in the combustion efficiency of the fuel gas, as a consequence of the deactivation of the oxygen carrier. The loss of reactivity depended on the H_2S concentration in the feed, although it could be considered almost negligible for low H_2S concentrations, i.e., below 100 vppm.

The oxygen carrier deactivation was due to the formation of nickel sulfide, Ni_3S_2 , which was detected in the solid samples at all operating conditions tested. According to thermodynamic calculations, this sulfide will be always formed in the fuel reactor when using nickel oxide as oxygen carrier due to the presence of CO and H_2 in the fluidized bed. However, despite the low melting point (1062 K) of the Ni_3S_2 , the sulfide formation did not produce any agglomeration problem during the whole experimentation time (≈ 35 hours with H_2S addition).

Sulfur added into the system was distributed between gas and solid species. SO_2 and H_2S were detected in the outlet stream of FR at very low concentrations (< 10 vppm). Another part of sulfur was released as SO_2 in the AR, and the rest was accumulated in the oxygen carrier as a form of sulfides and sulfates.

An important feature of the oxygen carrier used in this work, which was prepared by impregnation, was their regeneration capacity. When the H₂S feeding was stopped, the oxygen carrier recovered their initial reactivity with respect to CH₄ combustion.

Based on the experimental results obtained in this work, important conclusions about design and operation of industrial CLC plants were deduced. Considering both environmental aspects related with SO₂ emissions legislation and CO₂ quality requirements as well as operational problems derived from the oxygen carrier deactivation by the presence of sulfur, it can be concluded that fuels with sulfur contents below 100 vppm H₂S could be adequate to be used in an industrial CLC plant.

Acknowledgement

ACKNOWLEDGMENT. This research was conducted with financial support from the European Commission, under the 6th Framework Program, Contract no. 019800-CLC GAS POWER, by the CCP2 (CO₂ Capture Project), a partnership of BP, Chevron, Conoco-Phillips, Eni Technology, Norsk Hydro, Shell, Suncor, and Petrobras, and by Spanish Ministry of Science and Innovation (MICINN, Project CTQ2007-64400). C. Dueso thanks MICINN for a F.P.I. fellowship.

References

- (1) Intergovernmental Panel on Climate Change (IPCC). *Carbon Dioxide Capture and Storage*. Cambridge, United Kingdom and New York: Cambridge University Press. 2005. Also available from <http://www.ipcc.ch>.
- (2) Kerr, H. R. Capture and separation technologies gaps and priority research need. In *Carbon Dioxide Capture for Storage in Deep Geological Formations- Results from the CO₂ capture Project*. Vol. 1. Chapter 38. Oxford: Elsevier. 2005.
- (3) Lyngfelt, A.; Thunman, H. Construction and 100 h operational experience of a 10-kW chemical-looping combustor. In *Carbon Dioxide Capture for Storage in Deep Geological Formations- Results from the CO₂ capture Project*. Vol. 1, Chapter 36. Oxford: Elsevier. 2005.
- (4) Linderholm, C.; Abad, A.; Mattisson, T.; Lyngfelt, A. 160 hours of chemical-looping combustion in a 10 kW reactor system with a NiO-based oxygen carrier. *Int. J. of Greenhouse Gas Control* **2008**, doi:10.1016/j.ijggc.2008.02.006.
- (5) Adánez, J.; Gayán, P.; Celaya, J.; de Diego, L. F.; García-Labiano, F.; Abad, A. Chemical-looping combustion in a 10 kW_{th} prototype using a CuO/Al₂O₃ oxygen carrier: effect of operating conditions on methane combustion. *Ind Eng Chem Res.* **2006**, 45, 6075.
- (6) de Diego, L. F.; García-Labiano, F.; Gayán, P.; Celaya, J.; Palacios, J. M.; Adánez, J. Operation of a 10 kW_{th} chemical-looping combustor during 200 h with a CuO-Al₂O₃ oxygen carrier. *Fuel* **2007**, 86, 1036.
- (7) Ryu, H. J.; Jin, G. T.; Yi, C. K. Demonstration of inherent CO₂ separation and no NO_x emission in a 50 kW chemical-looping combustor: Continuous reduction and oxidation experiment. Proc. of the Seventh International Conference of Greenhouse Gas Control Technologies, vol. 2. Wilson, M.; Morris, T.; Gale, J. Thambibutu, K. (Eds.). Elsevier Ltd., Oxford, UK, p. 1907, 2005.

- (8) Mayer, K.; Pröll, T.; Bolhar-Nordenkamp, J.; Kolbitsch, P.; Hofbauer, H. Chemical Looping Combustion in a 120 kW test rig- First results. Proc. 9th International Conference on Fluidized Beds. Hamburg. Germany. 2008.
- (9) García-Labiano, F.; de Diego, L. F.; Adánez, J.; Gayán, P.; Abad, A.; Dueso, C.; Forero, C. R. Operation of a 500 Wth Chemical Looping Combustion plant using syngas as fuel. Proc. 2007 International Conference on Coal Science and Technology. Nottingham 2007.
- (10) Johansson, E.; Mattisson, T.; Lyngfelt, A.; Thunman, H. Combustion of syngas and natural gas in a 300W chemical-looping combustor. *Chem Eng Res Des.* **2006**, 84, 819.
- (11) Abad, A.; Mattisson, T.; Lyngfelt, A.; Rydén, M. Chemical-looping combustion in a 300 W continuously operating reactor system using a manganese-based oxygen carrier. *Fuel* **2006**, 85, 1174.
- (12) Abad, A.; Mattisson, T.; Lyngfelt, A.; Johansson, M. The use of iron oxide as oxygen carrier in a chemical-looping reactor. *Fuel* **2007**, 86, 1021.
- (13) Adánez, J.; Dueso, C.; de Diego, L. F.; García-Labiano, F.; Gayán, P.; Abad, A. Effect of Fuel Gas Composition in Chemical-Looping Combustion with Ni-based Oxygen Carriers. Part 2. Fate of Light Hydrocarbons. *Ind. Eng. Chem. Res.* (posterior paper)
- (14) Buckner, D.; Holmberg, D.; Griffin, T. Technoeconomic evaluation of an oxyfuel power plant using mixed conducting membranes. In *Carbon Dioxide Capture for Storage in Deep Geological Formations- Results from the CO₂ capture Project*. Vol. 1. Chapter 31. Oxford: Elsevier. 2005.
- (15) Hedden, D.; Stroud, H. J. F. Coal Gasification Processes. In *Chemistry of Coal Utilization*. Chapter 24. New York: John Wiley & Sons. 1981.
- (16) Sass, B.; Monzyk, B.; Ricci, S.; Gupta, A.; Hindin, B.; Gupta, N. Impact of SO_x and NO_x in flue gas on CO₂ separation, compression, and pipeline transmission. In *Carbon Dioxide Capture for Storage*

in Deep Geological Formations- Results from the CO₂ capture Project. Vol. 2. Chapter 17. Oxford: Elsevier. 2005.

(17) Bryant, S.; Lake, L. W. Effect of impurities on subsurface CO₂ storage process. In *Carbon Dioxide Capture for Storage in Deep Geological Formations- Results from the CO₂ capture Project*. Vol. 1. Chapter 18.

(18) Chen, I.; Shiue, D.-W. Resistivity to sulfur poisoning of nickel-alumina catalysts. *Ind Eng Chem Res.* **1988**, 27, 1391.

(19) Hepola, J.; Simell, P. Sulfur poisoning of nickel-based hot gas cleaning catalysts in syntehtic gasification gas. II. Chemisorption of hydrogen sulphide. *App Catal B:Environ.* **1997**, 14, 305.

(20) Hepola, J.; McCarty, J.; Krishnan, G.; Wong, V. Elucidation of behavior of sulfur on nickel-based hot gas cleaning catalysts. *App Catal B:Environ.* **1999**, 20, 191.

(21) Mattisson, T.; Johansson, M.; Lyngfelt, A. The use of NiO as an oxygen carrier in chemical-looping combustion. *Fuel* **2006**, 85, 736.

(22) Jerndal, E.; Mattisson, T.; Lyngfelt, A. Thermal analysis of Chemical-looping Combustion. *Chem. Eng. Res. Des.* **2006**, 84, 795.

(23) Wang, B.; Yan, R.; Lee, D. H.; Liang, D. T.; Zheng, Y.; Zhao, H.; Zheng, C. Thermodynamic investigation of carbon deposition and sulfur evolution in Chemical Looping Combustion with syngas. *Energy & Fuels* **2008**, 22, 1012.

(24) Gayán, P.; de Diego, L. F.; García-Labiano, F.; Adánez, J.; Abad, A.; Dueso, C. Effect of support on reactivity and selectivity of Ni-based oxygen carriers for chemical-looping combustion. *Fuel* **2008**, 87, 2641.

- (25) HSC Chemistry 6.1[®] 6.1. 2008. Chemical Reaction and Equilibrium Software with Thermochemical Database and Simulation Module. Outotec Research Oy.
- (26) Abad, A.; García-Labiano, F.; de Diego, L. F.; Gayán, P.; Adánez, J. Reduction kinetics of Cu-, Ni-, and Fe-based oxygen carriers using syngas (CO+H₂) for chemical-looping combustion. *Energy & Fuels* **2007**, 21, 1843.
- (27) Anheden, M.; Rydberg, S.; Yan, J. Consideration for removal of non-CO₂ components from CO₂ rich flue gas of oxy-fuel combustion. Proceedings of the 3rd meeting of the Oxy-fuel combustion network. Yokohama, Japan. March 2008.
- (28) Thambimutu, K. V. Gas Cleaning for advanced coal-based power generation. IEA Coal Research. 1993. IEACR/53.

List of Figures

Figure 1. Schematic diagram of the 500 W_{th} CLC prototype used for the tests with H₂S feeding.

Figure 2. a) Thermodynamic equilibrium for different H₂S concentration in the fuel gas. Fuel gas: 30% CH₄-70% N₂. NiO/CH₄ = 5. T_{FR} = 1143 K.

Figure 3. Thermodynamic equilibrium for different temperatures for addition of 300 vppm of H₂S. Fuel gas: 30% CH₄-70% N₂. NiO/CH₄ = 5.

Figure 4. Thermodynamic equilibrium for NiSO₄ decomposition.

Figure 5. Temperature and gas concentrations profiles for reference test 1. CH₄ = 30 %, T_{FR} = 1143 K, T_{AR} = 1223 K, u_{FR} = 0.1 m/s, G_s = 14 kg/h. H₂S = 500 vppm

Figure 6. Temperature and gas concentrations profiles for test 3. CH₄ = 30 %, T_{FR} = 1143 K, T_{AR} = 1223 K, u_{FR} = 0.1 m/s, G_s = 14 kg/h, H₂S = 300 vppm.

Figure 7. CO₂ concentration profiles during the tests with H₂S feeding.

Figure 8. SO₂ concentration obtained in the AR as a function of the H₂S fed. T_{AR} = 1223 K. (full symbols) T_{FR} = 1143 K, (white symbols), T_{FR} = 1103 K.

Figure 9. Thermodynamic equilibrium of sulfur compounds at different CO+H₂ concentrations. T_{FR} = 1143 K. CH₄=30%, H₂S=300 vppm.

Figure 10. CO₂ concentration at the FR outlet stream during the whole experimentation time.

Figure 11. TGA reactivity data for the fresh and regenerated oxygen carrier. T = 1223 K. CH₄ = 15% during reduction, air during oxidation.

Table 1. Main Characteristics of the Ni19- α Al:HI oxygen carrier.

NiO content (wt%)	19
Particle size (mm)	0.1-0.3
Particle density (kg/m ³)	2500
Mechanical strength (N)	4.3
Porosity (%)	41.7
Specific surface area BET (m ² /g)	6.8
Oxygen transport capacity	0.04

Table 2. Tests carried out in the 500 W_{th} CLC prototype using CH₄ with H₂S as fuel.

Test	T _{FR} K	T _{AR} K	CH ₄ vol.%	H ₂ S vppm	sulfides formation conditions (thermodynamic calculations)
0	1143	1223	30	0	
1	1143	1223	30	0 (500)	No
2	1143	1223	30	500	No
3	1143	1223	30	300	No
4	1143	1223	30	100	No
5	1103	1223	30	300	Yes
6	1143	1223	30	800 (1000)	Yes
7	1103	1223	30	300 (800)	Yes

Table 3. Mass balances of sulfur after 5 hours of continuous operation.

	Test 2	Test 3	Test 4	Test 5	Test 6	Test 6	Test 7	Test 7
Operating conditions								
T _{FR} (K)	1143	1143	1143	1103	1143	1143	1103	1103
T _{AR} (K)	1223	1223	1223	1223	1223	1223	1223	1223
H ₂ S fed (vppm)	500	300	100	300	800	1000	300	800
Sulfur distribution (%)								
IN	100	100	100	100	100	100	100	100
OUT gas FR ¹	5.3	9.1	15.4	4.9	2.9	3.0	11.3	12.2
OUT gas AR ²	42.8	47.3	23.4	0	69.3	74.4	16.4	12.4

1 Sulfur in FR was mainly present as H₂S, SO₂. Other sulfur compounds were also detected in the chromatograph in very small amounts.

2 Sulfur as SO₂.

Figure 1.

Figure 2

Figure 3

Figure 4

Figure 5.

Figure 6.

Figure 7.

Figure 8

Figure 9.

Figure 10

Figure 11