



Acid reactions in hub systems consisting of separate non-reactive CO₂ transport lines.

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Abstract

Corrosion in carbon steel pipelines is a major threat for safe CO₂ transport, and there have been several projects studying the corrosivity of impurities which could be found in captured CO₂. Often only two or three of these impurities have been present while performing the experiments. Although these experiments have delivered valuable knowledge, there are still questions of what happens when all impurities are present together. Furthermore, several transport pipelines may deliver CO₂ to a main pipeline through a hub system for storage or utilization, and while these streams may be safe individually, the blend in the main pipeline could create components that are hazardous for carbon steel.

The present study used a novel experimental setup to realistically simulate a CO₂ hub. Three individual “pipelines” were joined inside a glass tube in a transparent autoclave. The three “pipelines” were connected to three different reservoir pumps, simulating different capturing sources with dissimilar types of impurities. This gave a mix of low (ppmv) levels of oxygen (O₂), sulphur dioxide (SO₂), hydrogen sulphide (H₂S), nitrogen dioxide (NO₂), and water (H₂O). Three different experiments were performed with concentrations ranging from 5 to 35 ppmv of the impurities and a total pressure of 100 bar at 25 °C. All impurities were measured before and after the streams were mixed in the autoclave.

The experiments revealed that reactions between certain species were occurring even at concentrations as low as 5 ppmv, but the reaction products were not considered harmful. If the impurity concentrations were increased to about 35 ppmv, acids and solids were produced, and the situation became unacceptable for carbon steel.

Keyword: CCUS, CO₂, transport, CO₂ hub, impurities, specification test, H₂SO₄, HNO₃

1 Introduction

Carbon capture and storage is needed to meet the goal set by the International Energy Agency (IEA) [1] and the Intergovernmental Panel on Climate Change (IPCC) [2]. This will involve CO₂ capture, transportation, and permanent storage, and it is essential that the cost of the overall processes is kept as low as practically possible. Carbon steel is the only material that is economically feasible for long transport pipelines. However, the captured CO₂ may contain small amounts of additional components (called impurities in the present paper), which may be corrosive to carbon steel or cause operational problems. A quality specification for the CO₂ to be transported is therefore crucial to

ensure the integrity of the pipeline. Several CO₂ specifications have been suggested, but most of them have not been tested in realistic experiments. Consequently, the validity of these specifications is unclear. Some impurities (i.e. NO₂ and SO₂) have concentration limits based on health, safety, and environmental reasons, while possible chemical and corrosion reactions have not been considered. Reaction between many of these impurities is likely to occur [3], but the practical consequences have not been investigated in detail. Table 1 shows the large range of impurity limits that have been suggested in various literature sources [4-6].

Table 1. Expected impurities and concentration ranges from a review of 55 specifications [5], CO₂ is the balance.

| Compound | Concentration (ppmv) |
|------------------|-----------------------------|
| H ₂ O | 20 – 650 |
| O ₂ | 10 – 40000 |
| SO _x | 10 – 50000* |
| H ₂ S | 20 – 13000* |
| NO _x | 20 – 2500* |

*Often given as 100 ppmv for HSE concern.

Previous work from our research group [3,7,8] has shown that strong acids and elemental sulphur may form in CO₂ blends that are within established quality specifications [5,9]. The COORAL-project did also find traces of sulfuric acid and elemental sulphur in both gas and supercritical CO₂ experiments [10-12]. If these impurities react in the capture process they can most likely be removed before they enter the transportation system. However, it has been suggested that future transport projects will consist of multiple capturing sites which deliver CO₂ to a hub system with a main transport line, either as pipeline or by ships. One example of this is the full-scale CCS demonstration projects in Norway [13], where the captured CO₂ will come from three different capturing sites: a concrete factory, an ammonia plant, and a waste fuelled energy recovery plant. It is likely that these three CO₂ sources will have different impurity contents that may be unreactive within each individual stream, but reactions could occur at a later stage when the streams are mixed in the transportation network.

The aim of this study was to identify chemical reactions that are likely to occur in a realistic mix of impurities in CO₂ and/or verify if there is a safe operation window for transporting impure CO₂ in pipelines without creating a corrosive environment for the pipeline material. The impurities in Table 1 were split up in three different transport streams so the impurities could not react before the reaction chamber. In so, they represent three individual safe CO₂ stream without chemical reaction and corrosion. Mixing in a hub system was simulated by injecting these streams in an autoclave (reaction chamber). The present work applied a novel transparent autoclave that was built in-house. Reactions between impurities were studied visually and with high performance gas analysers.

2 Materials and methods

The experimental setup consisted of three parts; the reaction chamber (transparent autoclave) with camera, an impurity injection system, and the analysing module.

2.1 The reaction chamber

A transparent autoclave (Figure 1) was used as reaction chamber to allow in-situ visual observation of the experiment. The autoclave body was made of 316 stainless steel, and it had a volume of 330 ml with a maximum working pressure of 200 bar. The transparent windows consisted of soda lime glass (exposed to the CO₂ phase) and polycarbonate plates (exposed to air) which acted as pressure support for the lime glass. A magnetic stirrer was placed in the bottom of the autoclave to promote mixing of the CO₂ streams.

A T-shaped glass tube was placed inside the autoclave to simulate a CO₂ hub where three different streams were mixed. The first injection line delivered CO₂ with small levels (see Table 3, Table 4, and Table 5) of O₂, SO₂, and H₂O. The second stream contained CO₂ with H₂S and the third stream contained CO₂ with NO₂. Figure 2 shows the hub with the inlet tubes marked.



Figure 1: Transparent autoclave with camera and injection tubing.

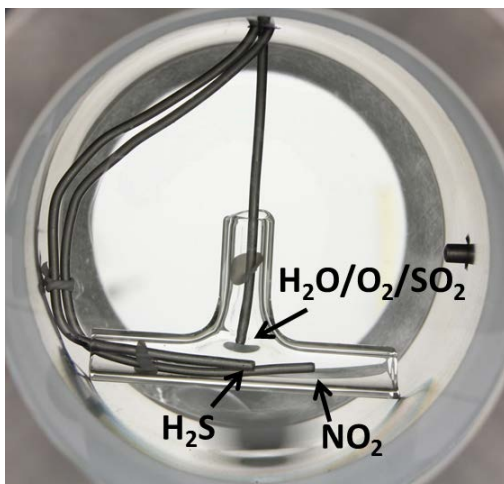


Figure 2: Glass tee tube (simulated CO₂ hub) with three individual injection lines. The glass tee was located inside the autoclave.

A camera was used to take still-images inside the autoclave, and a LED-lamp was used to achieve constant light conditions. Typically, one still image was taken every 10 minutes. The images were used to create videos showing the experimental development.

The temperature (25 °C) and the pressure (100 bara) were kept stable during all experiments.

2.2 Impurity injection system

The impurities were injected as pre-mixed solutions of CO₂ and the respective impurities. Three high precision piston pumps (266 ml volume) from Teledyne was used for this purpose. All pumps were held at a pressure slightly more than 100 bar. In addition, pure CO₂ (sometimes with H₂O) from a booster pump was also injected to the autoclave. The latter stream was controlled by a liquid pressure regulator that ensured a constant pressure of 100 bar. All four streams were injected at the same rates (about 25% each), but if one of the piston pumps was stopped, the pure CO₂ flow would increase correspondingly to maintain the pressure and the same total flow. The piston pumps needed to be filled with four times higher concentration since each pump represent one fourth of the flow. Thus, the concentration at the tip of the injection tubes and inside the glass tee was higher since the stream

had not yet been mixed (diluted) with the other streams. With the applied settings the piston pumps lasted about 24 hours before they had to be refilled.

The exhaust CO₂ was taken to a heated vaporizing regulator (to prevent hydrate formation and precipitation of impurities) where the pressure was reduced from 100 to 1 bar before the gas was sent to the analysing module. A mass flow controller from Bronkhorst was placed at the low-pressure side to regulate the exhaust flow rate. Normally this flow was about 0.85 g/min during the experiment.

The water content in the “pure” CO₂ stream could be adjusted at any concentration from nominally bottle dry to saturation by mixing dry CO₂ and CO₂ saturated with water at 25 °C at a desired ratio using a mini Cori-flow controller from Bronkhorst. Therefore, no liquid water was injected into the reaction chamber in these experiments, only water fully dissolved in CO₂.

2.3 Analysing module

The analysing module consisted of two multicomponent laser-based analysing systems (Emerson CT5400 and ap2e ProCeas) that were set in series to analyse the same gas. The system was configured in such a manner that either the exhaust CO₂ from the autoclave, or one of the individual CO₂ streams could be sent directly to the analyser module. Thus, the consumption of impurities could be detected as a measured difference in inlet and outlet concentrations. The CT5400 is a Quantum Cascade Laser (QCL) that could continuously analyse SO₂, NO, NO₂, N₂O, CO, and COS. The ProCeas is an Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS) that uses infrared laser to continuously measure H₂O, H₂S, and O₂. None of the analysers could handle a pressure of 100 bar so the pressure was reduced to about 1 bar prior to the analysis. The O₂ content was analysed with a XZR400 from Michell in the first two experiments (Hub01 and Hub02), while the laser based ProCeas was used for the last experiment (Hub3). The XZR400 has a zirconium oxide sensor with metallic sealed reference. The sensor could not be exposed to corrosive or flammable gases, so the sampling gas had to be scrubbed through a scavenger which removed SO₂, NO₂, and H₂S. The instrument was therefore located as the last analyser in the gas analysis line. It was sometimes observed that right after a new impurity injection was started, the O₂ signal was too low during a transient period, before it came back to the expected level. The exact reason for this not understood, but it could be related to remnants of impurities in the analysis system.

The accuracy of the analysers was about 1 percent of the full scale, which amount to about ± 1 ppmv for SO₂, NO₂, H₂S. While H₂O and O₂ had an accuracy of ± 3 ppmv. Since the measurements was performed at ambient pressure, ppm volume equals ppm mole at 25 °C and 1 bara. The analysers report concentrations in ppmv, therefore ppmv was used in this paper. When analysing the impurities from a 100 bar experiment it is important to remember that the reported ppmv are equal to ppm mole and the volume in ppmv is not related to the volume of the liquid CO₂ or the autoclave.

The heated vaporizing regulator could in theory trigger some additional reactions or precipitation since phase transition occurred at somewhat elevated temperature (45 °C). The solubility limits for acid and solids would also change in this environment due to the pressure transient through the regulator. This might give some deviation between the measured concentration at 1 bar and the real concentration at 100 bar.

Replacing the autoclave volume of liquid once took about 6.5 hours with the applied settings, and about 18 hours was needed to reach a stable impurity level (3 times volume replacement would give about 95% of the correct value). The sampling line from the autoclave to the analysers was made of 1/16” tubing, which gave a lag time of about 8 minutes.

2.4 Chemicals

Gas qualities used to make pre-mixed solutions of CO₂ are listed in Table 2.

Table 2. Gas qualities of impurities used in the experiments.

| Gas type | Purity (%) |
|------------------|------------|
| CO ₂ | 99.999 |
| NO ₂ | 99.0 |
| SO ₂ | 99.9 |
| H ₂ S | 99.8 |
| O ₂ | 99.999 |

2.5 Start-up procedure

After the glass tee tube was mounted and the autoclave was closed, the system was first purged with low pressure CO₂ (3 bar for one hour) and then high-pressure CO₂ (100 bar), to remove air and moisture from the autoclave. Previous experience has shown that moisture absorbs on the internal surfaces during installation. After the low-pressure purging process, the water concentration was typically around 50 ppmv. To reduce the concentration to an acceptable level of 10 ppmv, about five days with dry CO₂ at a flow rate of 0.85 g/min was required.

The impurity concentration of the stock solutions in the piston pumps was determined by running them one by one directly to the heated vaporizing regulator and then to analysing module. The injection rate of the piston pumps was fine-tuned to reach the target impurity level.

The sequence for impurity injection varied slightly from experiment to experiment. In the first experiment injection of all impurities was started at the same time, but in the other two experiments the injection was started consecutively one by one. For the latter case the order was somewhat different from experiment to experiment, but it was typically started by first injecting SO₂ and O₂ (first stream). Once the concentrations in the autoclave had stabilized, indicated by stable measurements of the exhaust gas, injection of the next impurity stream was started (often this was NO₂). After the values had stabilized, injection of the last impurity stream with H₂S was started. The order of impurity injection varied in order to detect any reactions that might occur with only two or three streams.

3 Results

Three experiments were conducted with three different concentration levels (5, 10 and 35 ppmv) of the key impurities. The concentration levels were given as what the concentration would be when mixed in the autoclave if no reactions occurred. The concentrations in the stock solutions were higher. These data are listed in the tables below (Table 3, Table 4, and Table 5).

3.1 Hub01 (5 ppmv)

This experiment was carried out with stock solutions in the 22 – 110 ppmv range. The target concentration inside the hub was 5 ppmv for SO₂, NO₂, and H₂S (see Table 3). The H₂S stock solution was unfortunately contaminated with water, resulting in much higher water levels than what was initially intended.

Table 3. Concentration of injected impurities in Hub01.

| Compound | Concentration in stock solutions | Theoretical concentration in autoclave |
|------------------|----------------------------------|--|
| | (ppmv) | (ppmv) |
| H ₂ O | 500 [#] | ~100 |
| SO ₂ | 40 | 5 |
| O ₂ | 110 | 12 |
| NO ₂ | 23 | 5 |
| H ₂ S | 22 | 5.5 |

[#]H₂S was contaminated with H₂O, giving a total content of about 500 ppmv.

The experiment was divided in two injection periods, the first was at 0 to 46 hours (Figure 3) and the second was at 116 to 164 hours (Figure 4). At 0 hours all impurities (all four streams) were injected at the same time (Figure 3). If no reactions occurred, then the concentrations should stabilize at the values given in Table 3 after some time (about 18 hours). This was not the case, based on the analysis results, suggesting that one or more reactions were occurring.

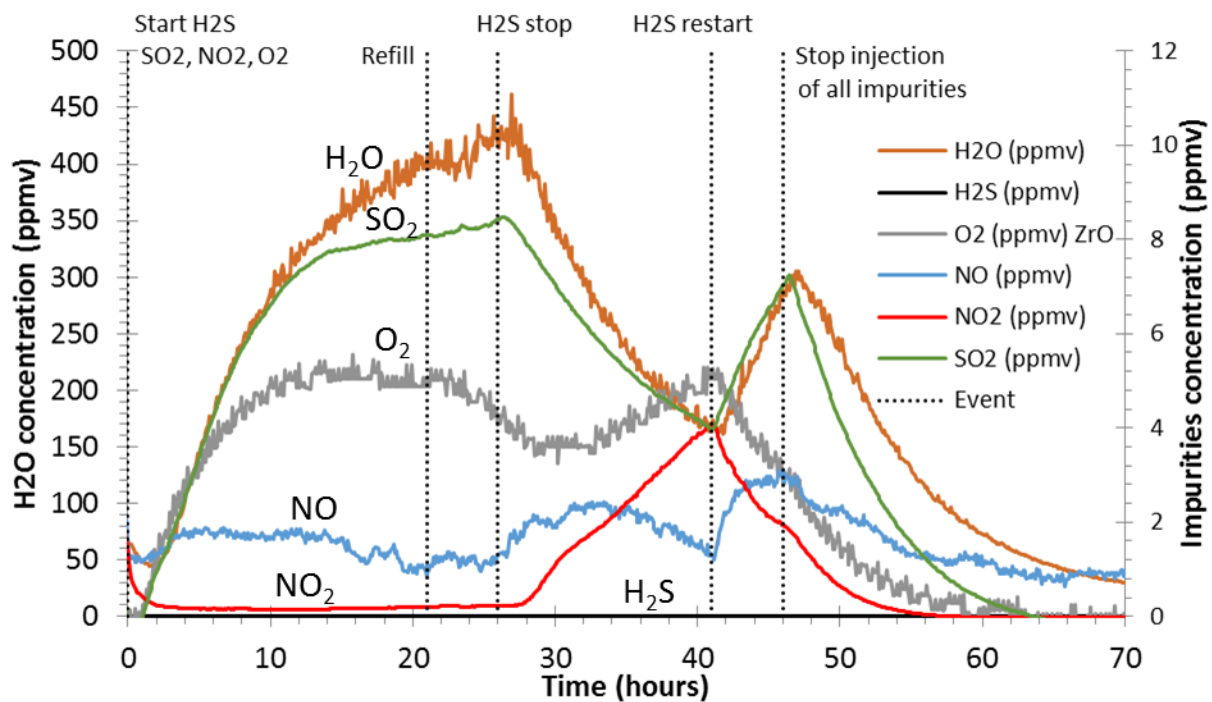


Figure 3: Exhaust gas analysis of Hub01, first injection period (0 to 46 hours).

The water content, mainly originating from the H₂S stock solution, increased as expected, but the rest of the impurities did not reach their target levels. H₂S was not detected at all. NO₂ was almost zero (about 0.2 ppmv) until the H₂S injection was stopped at 26 hours, after which NO₂ increased up to the target value. SO₂ was measured at higher concentrations than the target level and O₂ was much lower than the target level. SO₂ and O₂ impurities were injected from the same piston pump in a ratio of 1:3. NO was detected even if it was not injected. At 26 hours the H₂S injection was stopped and the system changed considerably, with a trend of all other impurities slowly changing towards the target (i.e. inlet) levels. The H₂S injection was started again at 41 hours, resulting in mostly the same situation as when H₂S was injected for the first time. One difference, however, was that the oxygen content was lower and continued to decrease towards zero. At 46 hours, injection of all impurities was stopped, and only pure CO₂ was injected.

The second injection period started at 116 hours (Figure 4). This time the impurity injections were not started at the same time. Injection of SO₂/O₂ was started first and when they stabilized, the H₂S injection was started (136 hours). To reduce the stabilization time for H₂S, it was injected at a higher rate for the first three hours, and then reduced to the correct set-point. At 143 hours the NO₂ injection was started, and the system changed character: SO₂ and NO increased while H₂S and O₂ decreased. NO₂ was not detected and at 154 hours O₂ and H₂S reached the lower detection limit. At 163 hours, injection of all impurities was stopped.

Still-pictures were taken repeatedly during the experiment (Figure 5). Some colour changes inside the chamber were observed, but no separate liquid phases or solids could be identified.

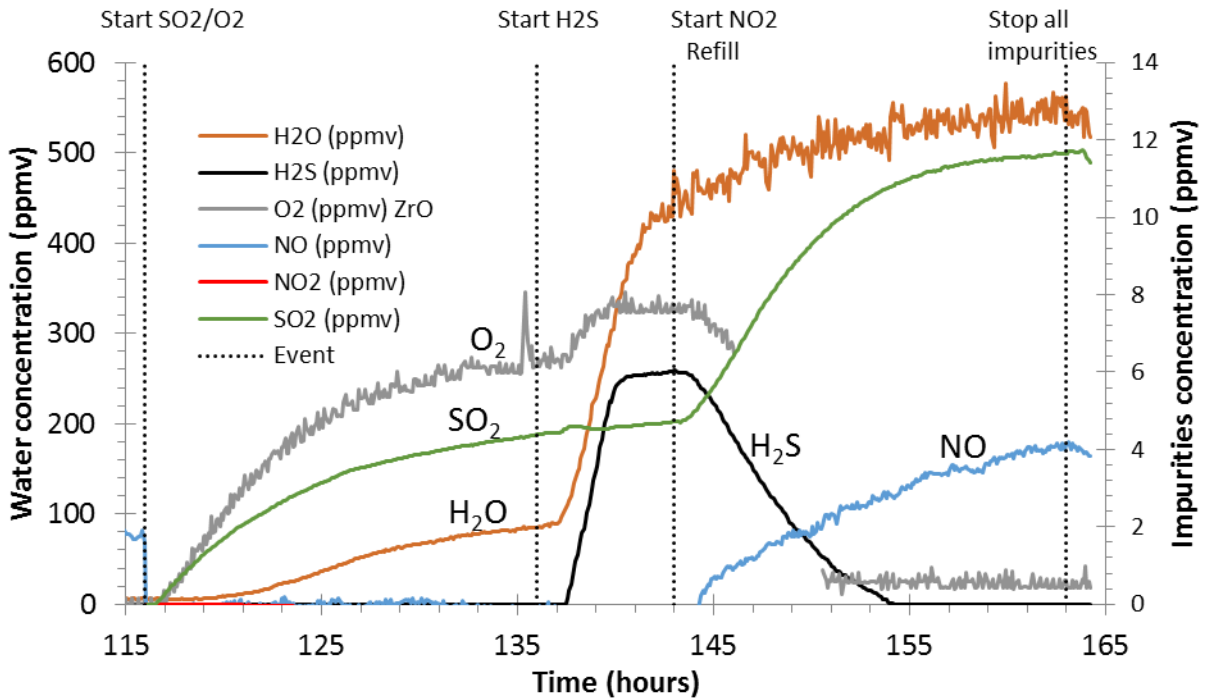


Figure 4: Exhaust gas analysis of Hub01, second injection period (115 to 165 hours).

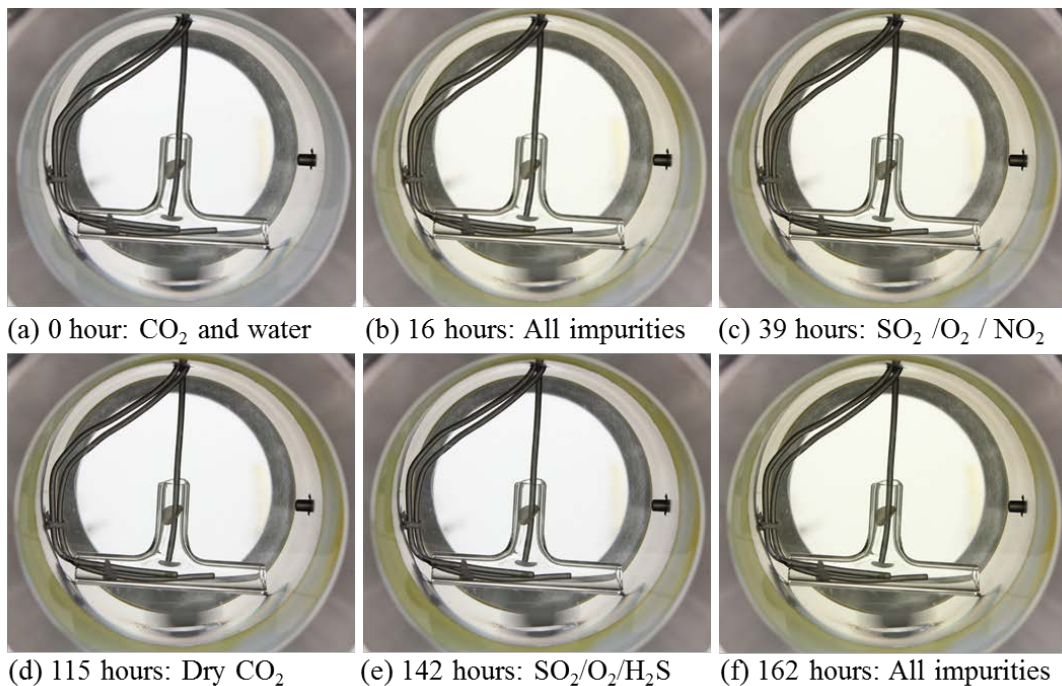


Figure 5: Still pictures taken during the first and second injection periods in Hub01.

3.2 Hub02 (10 ppmv)

The target values for this experiment were 10 ppmv for SO₂, NO₂, and H₂S. Table 4 shows the concentration injected (stock solutions) and the expected (theoretical) concentration after mixing, presuming that no reactions took place. The water content was initially high (about 250 ppmv) in this experiment, due to remnants of water in the impurity injection lines from a previous experiment.

Table 4. Concentration of injected impurities in Hub02.

| Compound | Concentration in stock solutions | Theoretical concentration in autoclave |
|------------------|----------------------------------|--|
| | (ppmv) | (ppmv) |
| H ₂ O | initially 220-270 | 35 |
| SO ₂ | 40 | 12 |
| O ₂ | 110 | 31 |
| NO ₂ | 60 | 10 |
| H ₂ S | 88 | 10 |

The experiment was started with injection of SO₂/O₂ (0 hours), and O₂ and SO₂ increased in the following period, see Figure 6. At 12 hours the injection rate of SO₂ /O₂ was temporarily increased (to reach the target faster), which caused an increase in the SO₂ /O₂ content. At the same time (12 hours) injection of H₂S was also started, and H₂S was detected shortly after. Injection of NO₂ was started at 19 hours, and this caused an increase of the SO₂ content to a stable plateau of about 20 ppmv while the H₂S content decreased to zero. The O₂ content increased intermittently before it decreased rapidly and after some time stabilised around 8 ppmv. This is not an expected behaviour and the reason for it is not quite understood. It could be caused by reactions in the wet scavenger compartment. In a test experiment (not shown) we confirmed that reactions involving oxygen can take place here. The oxygen in this and the previous experiment was measured with a zirconia sensor. This type of sensor is sensitive to flammable and corrosive gases, therefore the gas needed to be scrubbed before analysis. NO was detected after the NO₂ injection was started, and it increased slowly until the abrupt drop of O₂, after which it slowly decreased toward zero. NO₂ was detected after the abrupt O₂ drop, and it increased slowly with time.

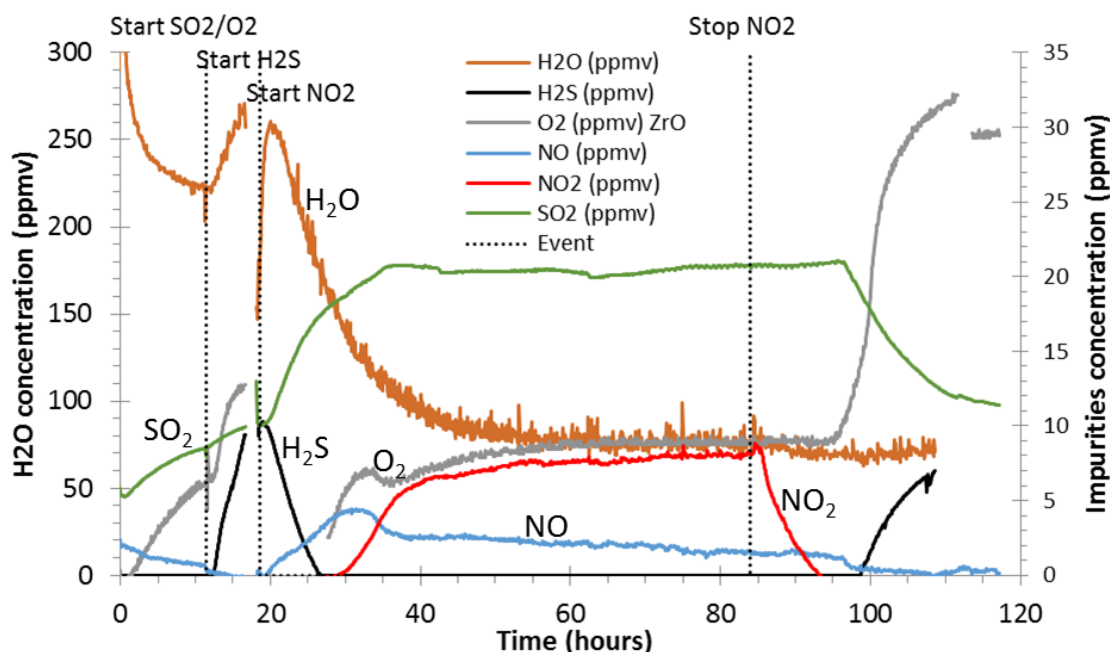
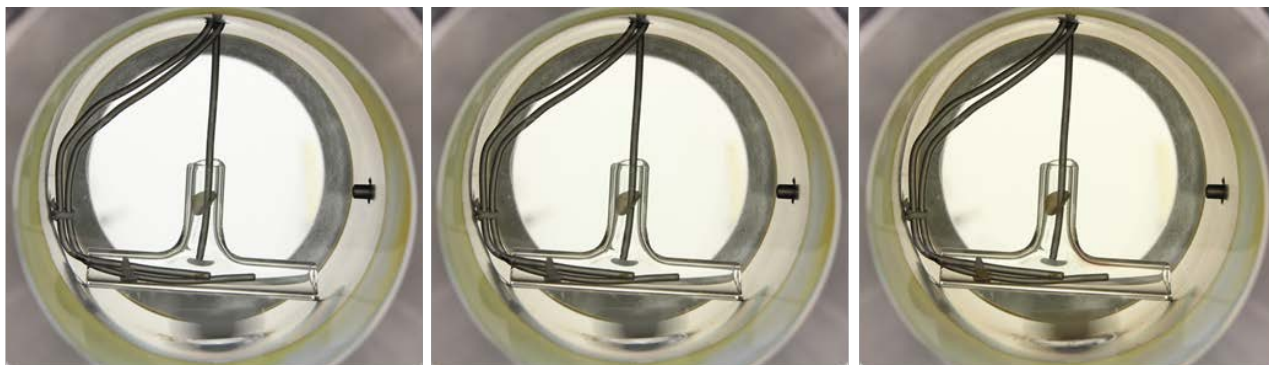


Figure 6: Analysis of exhaust gas from Hub02.

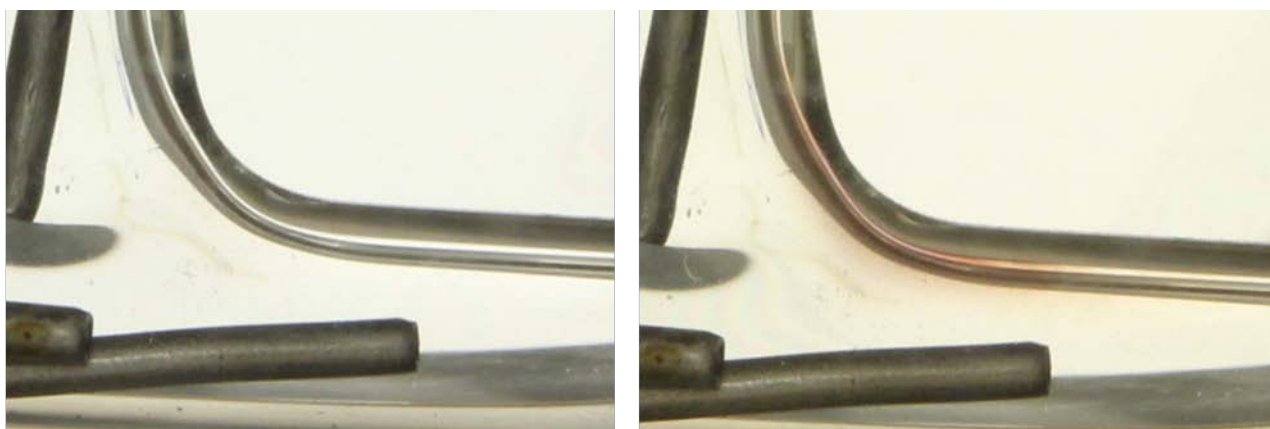
At 84 hours the NO₂ injection was stopped and at 108 hours the experiment stopped due to a failure of the analyser. Before this occurred, the concentration of the remaining injected impurities moved towards their target injection values.

Still pictures (Figure 7) taken during the experiment show colour change inside the chamber and in the lower right end of the glass tube there is some colour change at 62 hours (Figure 8).



(a) 16 hours: SO₂ /O₂ /H₂S (b) 26 hours: All impurities (c) 62 hours: All impurities

Figure 7: Still pictures taken during the injection period in Hub02.



(b) 26 hours: All impurities

(c) 62 hours: All impurities

Figure 8: Enlargement of still pictures in Figure 7, showing slight colour change of glass tube wall.

3.3 Hub03 (35 ppmv)

For the last experiment the target concentration for SO₂, NO₂, and H₂S was increased to about 35 ppmv. There was some water contamination in the injection system, resulting in a water content of about 120 ppmv. Table 5 sums up the stock and expected solution concentrations.

Table 5. Concentration of injected impurities in Hub03.

| Compound | Concentration in stock solutions | Theoretical concentration in autoclave |
|------------------|----------------------------------|--|
| | (ppmv) | (ppmv) |
| H ₂ O | 120 | 120 |
| SO ₂ | 370 | 38 |
| O ₂ | 890 | 95 |
| NO ₂ | 200 | 26 |
| H ₂ S | 300 | 41 |

SO₂ and O₂ was injected first, see Figure 9, and after about 20 hours the injection of NO₂ was started. This led to a decrease in the O₂ concentration. To verify that this decrease was real, the SO₂/O₂ stock solution was routed directly to the analyser (shown as discontinuous lines in Figure 9 between 41 to 45 hours), and it proved that the oxygen consumption was real. H₂S was introduced to the system at 51 hours, and an immediate change in impurity concentrations was observed. The water concentration increased together with SO₂. At the same time, O₂ decreased rapidly while, NO₂ decreased slowly. H₂S was not detected until 10 hours after the NO₂ injection was stopped at 101 hours. The system then slowly reverted back to the original target values. When H₂S was stopped at 134 hours the system was not affected, except for the decrease in water because contaminant water was injected together with H₂S. Finally, injection of O₂/SO₂ was stopped after 145 hours.

Still-pictures (Figure 10) acquired during the experiment showed that both, colour change, and precipitation of liquids and solids occurred inside the autoclave. The glass tee went from clear to yellow, then some solids and later liquids formed, and in the end the glass tube turned opaque. The first sign of precipitation occurred at 52 hours (Figure 9) about 1 hour after the H₂S injection started, observed as blackening of the bottom glass tee (Figure 10). At 53 hours the first sign of dew occurred on the centre tube in the glass tee, and both the black deposits and the dew were clearly visible at 62 hours (picture c in Figure 10). At 65 hours the first sign of droplet formation became visible, and after this the liquid accumulated fast. The view became impervious after NO₂ was stopped. The liquid inside the autoclave was analysed using ion chromatography after the experiment. Both SO₄²⁻ and NO₃⁻ were detected, which most likely originated from sulfuric acid and nitric acid formed during the experiment. The molar ratio was about 10:1 of SO₄²⁻ (sulfuric acid) to and NO₃⁻ (nitric acid). At about 68 hours the NO₂ pump was refilled with a more dilute stock solution with a theoretical concentration of 20 ppmv NO₂. This could explain some of the decrease occurring at this time.

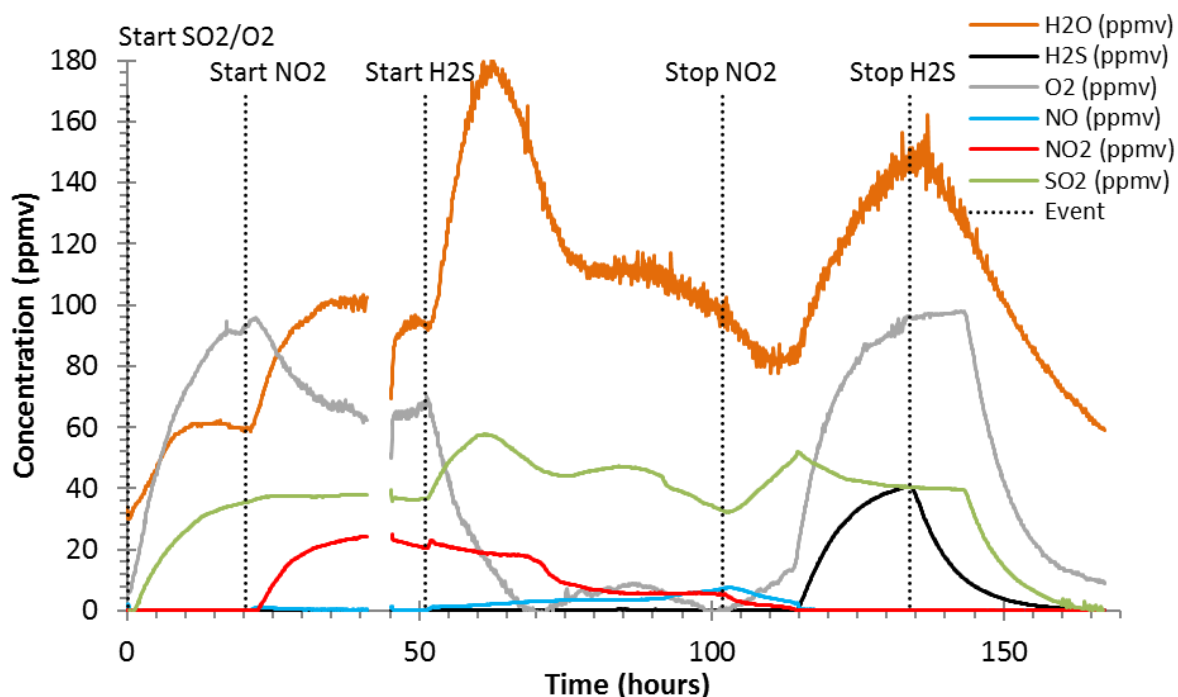


Figure 9: Analysis of exhaust gas from Hub03.

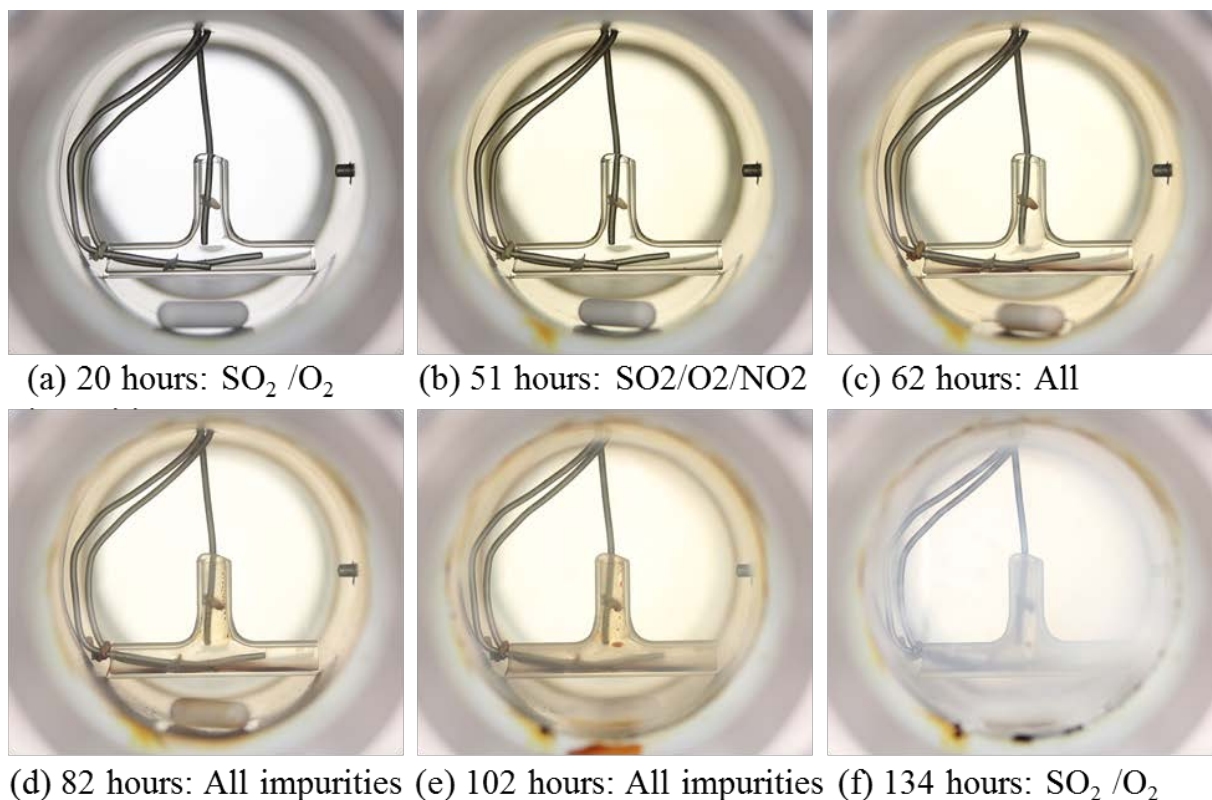


Figure 10: Still pictures taken during the injection period in Hub03.

4 Discussion

In summary, the present test campaign has demonstrated that chemical reactions occur for certain blends of impurities. However, not all blends caused reactions and not all reaction products formed corrosive species. When corrosive species did form, the amount increased with increasing impurity content.

4.1 Fully dissolved reaction products

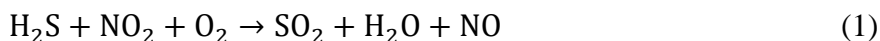
The first experiment (Hub01) clearly showed (Figure 3) that several reactions occurred when all impurities were introduced simultaneously, since none of the impurities reached their target concentrations. However, because all impurities were introduced at the same time it was difficult to identify possible individual reactions. The impurities were therefore added sequentially for the rest of the work.

In the second injection period of Hub01 there were no reactions until NO_2 was introduced, demonstrating that a mixture with H_2S , H_2O , SO_2 , and O_2 was stable under these conditions. This contrasts with observations in other systems, where reaction of H_2S and O_2 have been reported [14-17]. When the NO_2 injection was started the second time (143 hours in Figure 4), indication of reactions became clear. The H_2S content decreased at the same amount as SO_2 increased. Another interesting observation was that the O_2 content was reduced and after some time fully consumed. The new species NO was detected, while the NO_2 level was at the detection limit. These trends were also observed in the other experiments, except that O_2 did not completely disappear in Hub02 and Hub03, and the measured NO_2 concentration was then higher. There was not much difference if NO_2 was injected before H_2S or vice versa, both had to be present simultaneously for reactions to occur.

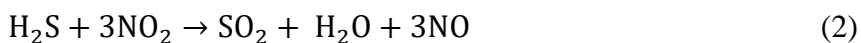
A more detailed study of the measured and theoretical impurity content is shown in Figure 11 and Figure 12. The theoretical concentration is the calculated concentration if no reactions occurred (injection and dilution). With exception of Hub03, where liquid acid precipitated, the SO_2 analysis was close to the sum of SO_2 and H_2S that was injected, clearly proving that all H_2S was converted to

SO₂ in the presence of NO₂. It can also be observed that NO₂ was present in the exhaust feed only if O₂ also was present. Furthermore, if no liquid acids were formed, the sum of NO and NO₂ was always the same as the injected NO₂ level.

It was demonstrated multiple times that H₂S, O₂ and SO₂ can coexist (at least up to about 35 ppmv) together with water without reactions taking place, suggesting that NO₂ is a very important reactant under these conditions. These observations lead to the proposal of the following reaction:



H₂S, NO₂ and O₂ react to produce SO₂, H₂O and NO. This is very clear in the second period of Hub01. It should be stressed that this is assumed to be the overall reaction, not including possible intermediate reactions. However, there are several indications that reaction 1 is not occurring under all conditions. For example, in Hub02 after the NO₂ injection was stopped, the SO₂ level continues to remain high for many hours (green and blue lines in Figure 11b) until NO/NO₂ has been removed from the system, after which the other impurities go back to their injection levels. This could indicate that H₂S does not react directly with O₂, but rather with NO₂. If H₂S and O₂ could react directly, the SO₂ level should have remained high also after NO₂ had been removed from the system. Apparently even low concentrations of NO₂ is enough to oxidise H₂S. It is therefore suggested that the following reactions can occur either in parallel with, or instead of, reaction 1:



Thus, it is suggested that NO₂ is acting as an oxidation agent for H₂S to form NO, SO₂ and H₂O, while O₂ reacts with NO to form NO₂ that again can react with H₂S. Clear indication of this is shown in Figure 11b, where the SO₂ level (green line) continues to remain high until NO/NO₂ is completely removed from the system, after which H₂S and SO₂ returns to their injection levels. If NO₂ was not needed to oxidize H₂S, the SO₂ should have followed the dashed blue line, which would represent dilution of already reacted H₂S. Further support for this is the fact that NO₂ is only detected if also O₂ is present in the exhaust gas. Since the SO₂ content follows the injection levels of the reactants to an almost perfect fit of the theoretical values (Figure 11 and Figure 12), it must mean that the reactions (1 - 3) are fast compared to the residence time (approximately 18 hours).

However, there is some discrepancy for the oxygen analysis. Apparently, more O₂ is consumed than what can be accounted for with reactions 1 - 3. Some of this is most likely related to analytical challenges (see section 2.3), but it could also be related to production of certain species that were not analysed for. When NO₂ was introduced to the system there were always observed some irregularity with the oxygen analysis. This could indicate that some form of reaction between O₂ and NO/NO₂ is taking place and producing some unidentified species.

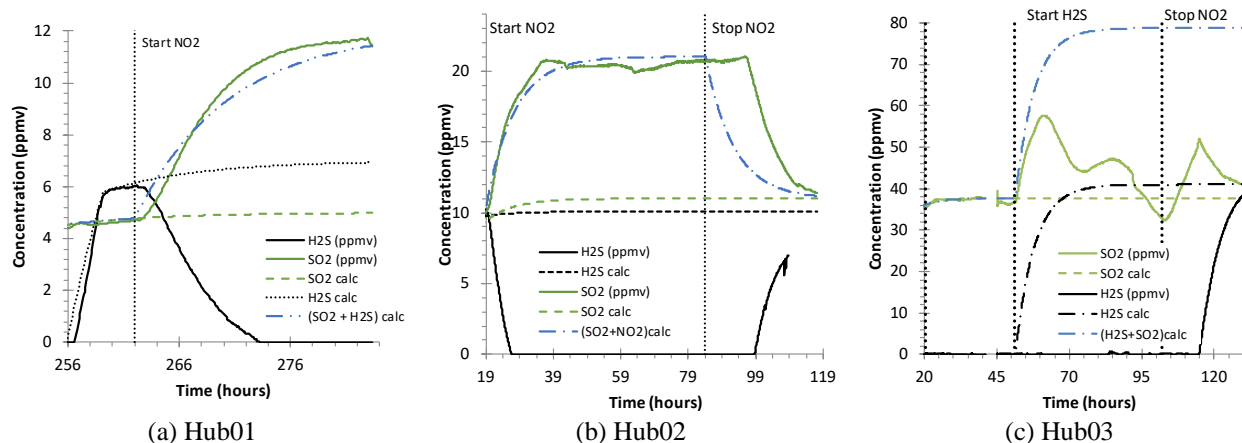


Figure 11: Analyzed SO₂ (solid green lines) and analyzed H₂S (solid black lines) compared with the theoretical compositions (dashed lines) and the sum of the theoretical compositions (dashed blue lines).

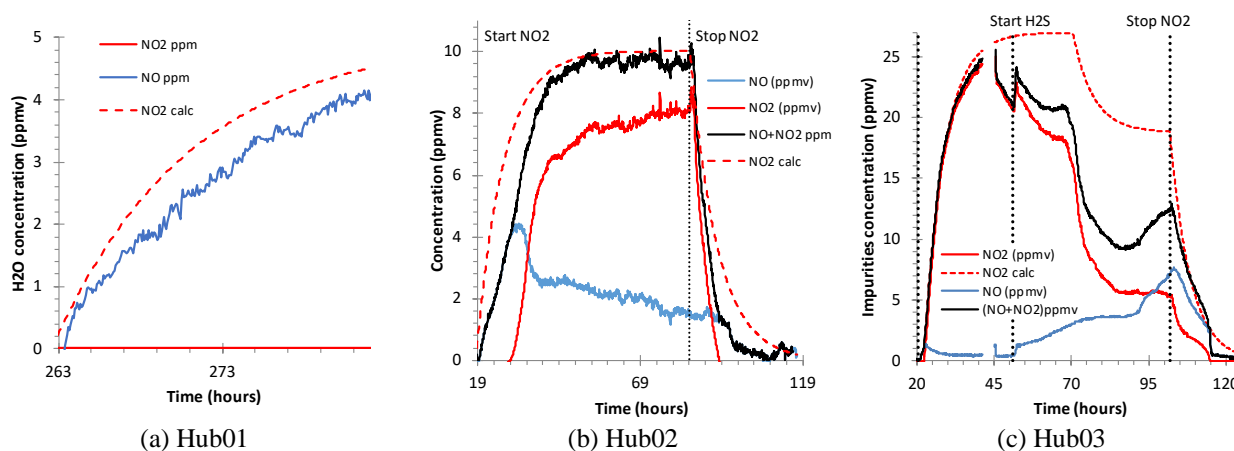
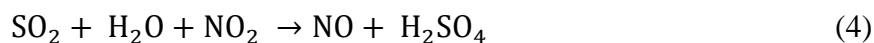


Figure 12: Comparison of analyzed NO₂ (red solid line) and NO (blue solid line) compared to the theoretical NO₂ concentration (red dashed lines) if no reactions occurred. The black line is the sum of NO₂ and NO.

4.2 Precipitated reaction products

Even though most of the reactants and products could be accounted for in the experimental campaign (see the previous paragraph), additional precipitated products were visually observed in Hub02 and Hub03. In Hub02 there was just a slight blackening of the glass tee, and the small amount of product that formed was not enough to be analysed. However, in Hub03 (Figure 9) there was clear formation of liquid products (Figure 10) and ion chromatograph analysis showed that these contained SO₄²⁻ and NO₃⁻. Most likely this was sulfuric acid (H₂SO₄) and nitric acid (HNO₃), as also observed in previous work [3,12], but it could in principle also be H₂SO₃ or HNO₂ acids that were further oxidised by air during sampling or by the aqueous eluent in the IC column during analysis. However, H₂SO₃ cannot exist in solution [18] and HNO₂ cannot exist in gas phase [19]. Thus, the observed precipitate in the Hub03 is probably H₂SO₄ and HNO₃. The first sign of “dew” occurred shortly after the injection of H₂S started (53 hours in Figure 9). Interestingly, the first sign of larger brown droplets was just after both SO₂ and H₂O started to decline. In addition, the SO₂ concentration never reached the sum of SO₂ and H₂S injected (which was 79 ppmv, see Figure 11c). Instead it peaked at 57 ppmv, meaning that after 60 hours, reaction 1 or 2 were not the only reactions in this experiment. When both SO₂ and H₂O started to decrease (62 hours in Figure 9), the amount of produced liquid precipitation visually increased in the reaction chamber. By using the fact that both SO₂ and H₂O decreased significantly, and NO₂ also decreased slightly while NO increased slowly, the following reaction is suggested:

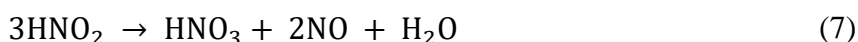
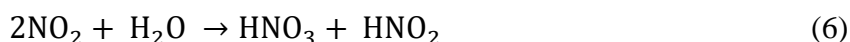


In-house data, which will be included in a later publication, have shown that the solubility of sulfuric acid in dense phase CO₂ may be as low as 1 ppmv suggesting that the “dew” and the first liquid

observed on the glass tee was H₂SO₄ that had precipitated since the solubility limit was exceeded. The formation of nitric acid could be through many different routes, such as:



However, equation 5 is not favourable based on standard Gibbs energy, with a positive value of 15.3 kJ/mol for gas phase reaction and 9.4 kJ/mol for liquid phase reaction (data in dense phase CO₂ are not available). Instead it is proposed that NO₂ reacts to nitrous and nitric acid in an aqueous solution. Since sulfuric acid is highly hygroscopic, it will absorb water from the CO₂ phase and thus provide the aqueous solution needed for the disproportionation of NO₂. The reactions would then be:



As shown previously, NO can be re-oxidized by O₂ to NO₂, therefore the overall reaction suggested by our data, would be:



The ratio of 10:1 between sulfuric acid and nitric acid could reflect the amount of water available through absorption for reaction 6, but in-house data (to be published) show that the solubility of HNO₃ in dense phase CO₂ is 3 orders of magnitude higher than H₂SO₄. Thus, the nitric acid could be dissolved in the CO₂ and transported out of the autoclave. In fact, HNO₃ was frequently detected inside the heated vaporizing regulator on the exhaust line. Consequently, the ratio between those acids cannot be used as measure of the production ratio of these acids.

4.3 Estimation of produced species

The difference between the theoretical concentration and the measured concentration can be used to predict how much of the acids or other compounds that were produced in Hub03 (Figure 13). Since the concentrations are ppm volume at 1 bar and 25 °C which are equal to ppm mole, the concentration can be used directly to determine the amount of the produced species. From 20 – 50 hours there is a drop in the oxygen content that is not fully understood, but it is assumed to be an analytical artefact since the SO₂ and NO₂ content followed the theoretical curves for non-reactive conditions. There are not any other reactions occurring before the injection of H₂S started.

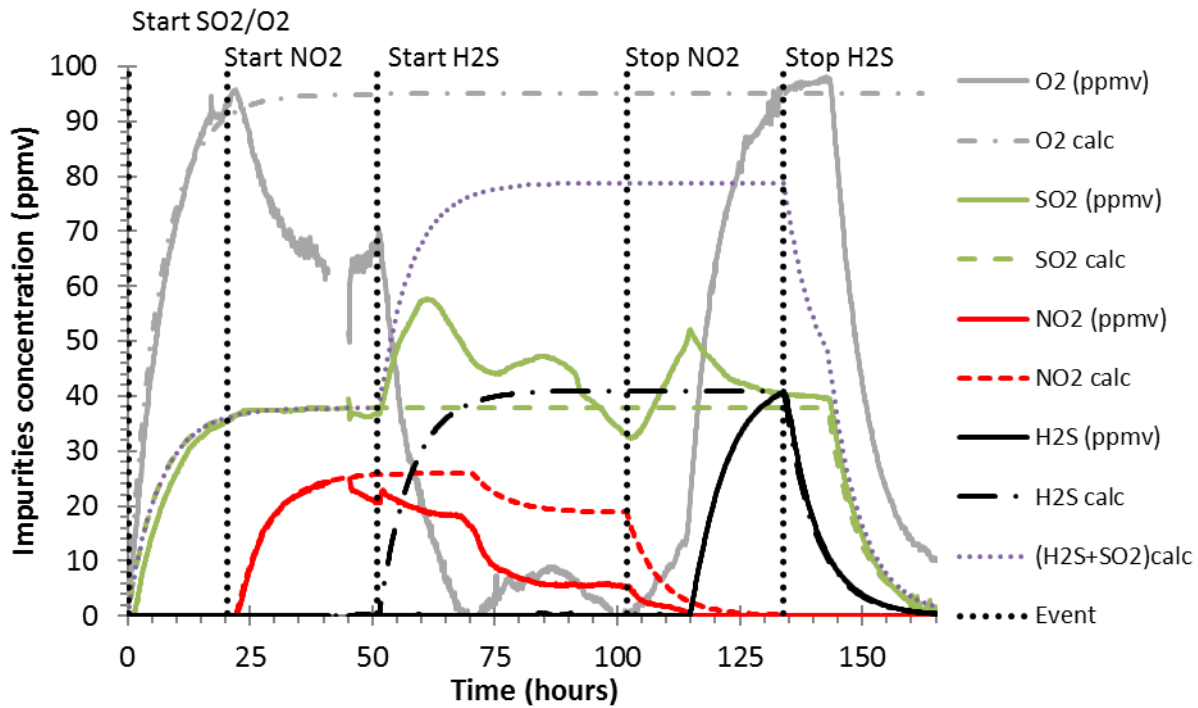


Figure 13: The difference between theoretical (dashed lines) and measured (solid lines) impurities for Hub03.

Certain species like the strong acids (H_2SO_4 , HNO_3), H_2 and some nitrogen oxides were not analyzed in the present work. An accounting (element balance) for all species that were injected and analyzed in the exhaust CO_2 (Figure 13) was therefore carried out to try to give a rough estimate of the amount of produced components (the precipitated liquids/solids). Formation of H_2SO_4 , would need the consumption of 2 x H, 1 x S, and 4 x O, likewise, HNO_3 formation will consume 1 x H, 1 x N and 3 x O. Consumed elements is basically the difference between the injected (theoretical) and the measured concentration. The elements available to produce acids can be found in Figure 13. For example, at 75 hours the difference between injected O_2 and measured O_2 was 90 ppmv (equal to 180 ppmv “O-consumed”). The difference between injected H_2S and measured H_2S was 40 ppmv, which gives 80 ppmv “H-consumed” and 40 ppmv “S-consumed”. As for SO_2 , there was no consumption but instead about 6 ppmv was produced. This gives negative numbers of -6 ppmv sulphur and -12 ppmv of oxygen.

The elemental balance for of all injected and analyzed species are summarized in Figure 14a. The calculations showed that formation of both acids was limited by the excess of N and S, most of the time (i.e. H and O excess concentrations were larger than the equivalent excess N and S content). Figure 14b shows the balance for production of H_2SO_4 and the lower line was the limiting reactant. Figure 14c shows the balance for production of HNO_3 after H_2SO_4 was produced first (b) and again the lowest line would be the limiting reactant. These calculations show that hydrogen was the limiting reactant in the period between 55 and 65 hours, partly preventing formation of H_2SO_4 and HNO_3 . The reason for the low amount of hydrogen was the production/emission of H_2O in this period (55 to 65 hours in Figure 9). Still there was a consumption of sulphur, and this could indicate the formation of elemental sulphur. Precipitates were observed in the bottom of the glass tee in Figure 10 after 62 hours. In Figure 14 it was assumed that sulfuric acid is first product and that nitric acid was produced from the excess compounds (after sulfuric acid was produced). For simplicity it is assumed that these assumptions are valid throughout the whole set of calculations.

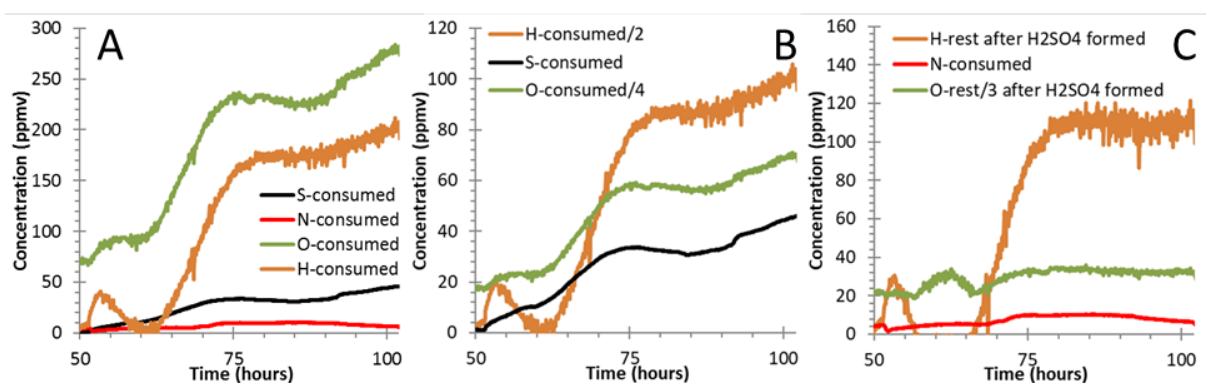


Figure 14: Calculation of the amount of possible produced acids during Hub03. The diagram to the left (A) shows the balance of all elements involved. The diagram in the middle (B) shows the matching of sulfuric acid. The diagram to the right (C) shows matching of HNO₃ after sulfuric acid is produced (in B).

The estimated product produced during the experiment between 50 and 100 hours is shown in Figure 15. There is some excess oxygen after the formation of the strong acids and elemental sulphur. There could be several reasons for this excess. First, the water contaminated impurity injection system would represent some uncertainty regarding the water feed. Analytical deviations could also contribute to less accurate calculations, especially regarding O₂, which decreased when the NO₂ injection was started at 20 hours (Figure 9) in Hub03. The shown O₂ analysis was carried out using a high-performance laser analyser, while at the same time also a zirconia-based oxygen analyser was connected (results not shown for Hub03). The zirconia-based sensor can be damaged by NO₂ and H₂S, so the gas was always routed through a scavenger first, before the gas entered the zirconia analyser (this analyser is the last instrument in low pressure the analysis line). The zirconia-analyser however, did not detect the decrease of 30 ppmv oxygen during 25 – 50 hours in Hub03, in fact the oxygen moved towards the target value. This could indicate that some unknown process that consumed O₂ occurred during this period and that this reaction was reversed in contact with the scavenger.

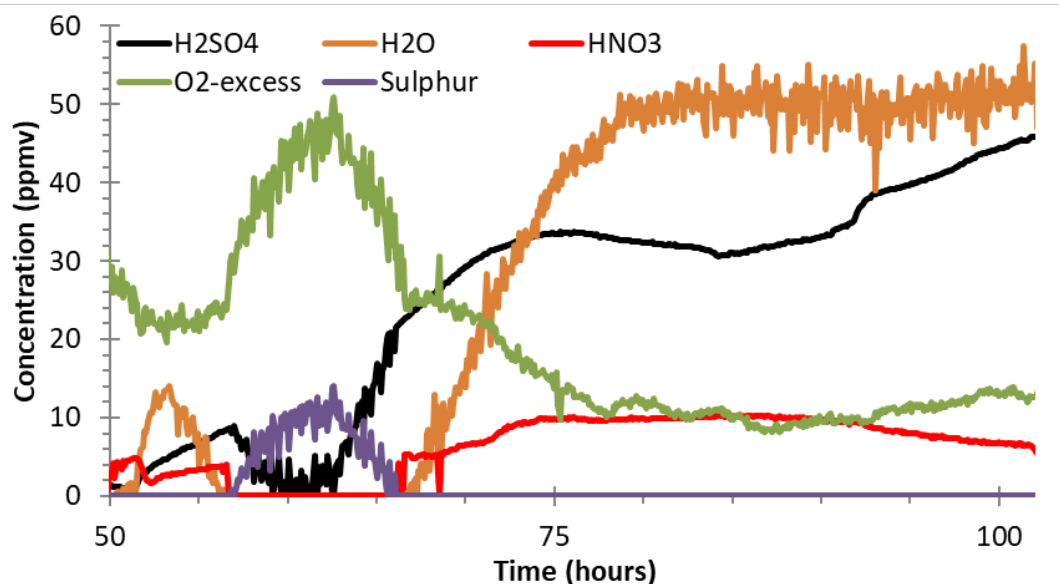


Figure 15: Estimate of the amount of produced species.

The analyses of the precipitate after the experiment showed that sulfuric and nitric acid were formed, but exact quantification was not possible. The calculations show that sulfuric and nitric acid were produced at a maximum average concentration of 44 and 11 ppmv, respectively. The solubility limit of sulfuric acid was therefore exceeded according to in-house data, meaning that sulfuric acid would precipitate and form a liquid phase, which was indeed observed. Nitric acid, on the other hand, was always present well below its solubility limit in pure CO₂, meaning that most of it was transported

away with the vented CO₂. However, HNO₃ was also present in the liquid precipitates, indicating that the reaction took place in the newly formed liquid phase.

4.4 CO₂ transport specification

The results presented in the present paper clearly show that, when present in more than 35 ppmv, these impurities do create corrosive reaction products (strong acids) which is not acceptable for carbon steel pipelines. Even though no corrosion coupons were exposed in the present work, it is well known that HNO₃ and H₂SO₄ are corrosive for carbon steel. Thus, a CO₂ specification should not allow for these impurities to be present at values as high as 35 ppmv. According to the present results, an acceptable impurity level should be somewhere between 10 and 35 ppmv if H₂S, NO₂, SO₂, and O₂ are present. Another approach could be to completely remove one of the reactants. Removal of NO₂ is probably the best solution, but it should be noted that the present results indicate that even small amounts of NO₂ could start reactions. The only reaction that actually removes NO₂ from the CO₂ bulk phase is the production of HNO₃. In the production of sulfuric acid, NO₂ acts somewhat like a catalyst and is not part of the overall reaction in Equation 4. Thus, just slight NO₂ could trigger formation of H₂SO₄ which may cause severe corrosion. Interestingly, the major acid formation started when H₂O and SO₂ reached about 180 and 60 ppmv, respectively. This could indicate that there is a threshold level above which production of acid starts. Hub01 and Hub02 had much higher H₂O concentrations, but the SO₂ content was ≤ 20ppmv and no acids were observed. This could indicate that the acceptable SO₂ level is somewhere between 20 and 60 ppmv. Since H₂S may react to form SO₂, it would probably be best to use the sum of H₂S + SO₂ as the limiting level for these impurities.

Reactions occurred also in the experiments with 5 and 10 ppmv, but since the reaction products remained fully dissolved in the CO₂ phase they are probably not corrosive for the carbon steel pipeline. If they precipitate later in the pipeline, e.g. at other temperatures or pressures, corrosive phases could form and be a threat to the pipeline. Further work should be carried out to study the corrosiveness of the products of the reactions at 5 and 10 ppmv.

5 Conclusion

When separate CO₂ streams with water, O₂, SO₂, H₂S, and NO₂ were mixed to simulate a CO₂ transportation hub system, reactions were observed. The types of products that formed were concentration dependent, and no corrosive species were observed for the lowest impurity concentrations (5 and 10 ppmv). A separate liquid phase containing H₂SO₄ and HNO₃ formed when the impurity concentration was 35 ppmv of SO₂, NO₂, and H₂S. An impurity concentration of 10 ppmv and lower resulted in reactions, but the products were not corrosive and did not form a separate liquid phase and are therefore not considered a threat for carbon steel. Thus, a safe operation limit for these impurities will be somewhere between 10 and 35 ppmv of SO₂, NO₂, and H₂S.

6 Acknowledgements

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