1. Introduction

In the blast furnace of a steel mill the iron ores are reduced to metallic iron. The off-gas from this process contains carbon monoxide (20–28%), carbon dioxide (17–25%) and hydrogen (1–5%). The resulting calorific value of the blast furnace gas is in the range of 2.7 MJ/m³ (STP) to 4.0 MJ/m³ (STP). Therefore, the blast furnace gas is used as a fuel in hot blast stoves, boilers and other burners. For the trouble-free burner operation a low dust concentration in the blast furnace gas is required.

The temperature of the top gas leaving the blast furnace is usually between 100°C and 200°C and the dew point is in the range from 35°C to 50°C. In some cases the gas temperature is beyond these limits, e.g. during start-up of the blast furnace or when irregularities in the charging occur. Temperature peaks up to 600°C are possible.

The dust emissions of a blast furnace and the separation efficiency of the top-gas scrubber were investigated for the gaseous components HCl, H₂S, SO₂, COS, CS₂, CH₃SH, HCN and NH₃. The clean gas emission of sulphur was dominated by COS which accounted for about 85% of the total sulphur emissions. From the hydrogen halides only HCl was present above the detection limit and the concentrations of NH₃ and HCN were low. The average separation efficiency for HCl, SO₂ and NH₃ was 96%, 81% and 46%, respectively. COS was not separated in the scrubber system. The concentrations of the weak acids HCN and H₂S were higher in the off-gas after the scrubber compared to the concentration before the scrubber. This phenomenon was explained by the release from the scrubber water into the gas of un-dissociated H₂S and HCN originating from cyanides and sulphides contained in the separated dust. Separation efficiencies similar to those of the scrubber system are expected to be achieved also by dry sorption gas cleaning processes. However, this has to be verified in experiments. In the case of applying a dry gas cleaning system, the concentrations of H₂S and HCN in the clean gas would be even less.

KEY WORDS: blast furnace; gas cleaning; hydrogen cyanide emission; hydrogen sulphide emission.
shows a typical process flow diagram of a two-stage blast furnace gas cleaning system. The gas coming from the blast furnace \( \dot{G}_{\text{in}} \) is cleaned in the first de-dusting stage (1). There the coarse dust is separated from the gas and discharged as a dry residue \( \dot{R}_{\text{t}} \). After de-dusting in the scrubber (2) the blast furnace gas is expanded in the top gas recovery turbine (3) and sent on for further utilization \( \dot{G}_{\text{out}} \). In the scrubber system also water-soluble gaseous pollutants such as ammonia and hydrogen chloride are separated from the top-gas. The collected dust is separated from the scrubber water by sedimentation (4). The pressure loss of such a gas cleaning system is in the range of 10 kPa to 30 kPa and the outlet temperature of the top-gas gas is 55°C to 65°C.

In recent years, mainly in China, fabric filters were installed frequently for second stage de-dusting of blast furnace gas. The dry de-dusting process offers several advantages. First, a downstream top gas recovery turbine provides a higher energy output due to the higher temperature of the purified blast furnace gas and lower pressure drop of the cleaning system. Secondly, treatment of scrubber waste water is not required and, thirdly, the residue from the de-dusting is available as a dry powder, which makes handling and further utilization much easier. For example, the separation of the zinc-enriched fines fraction can be done in a scrubber quite well. While remaining components such as ammonia and hydrogen chloride which can be separated in a scrubber quite well. Particularly hydrogen chloride is problematic in purified blast furnace gas with regard to corrosion of the gas pipes and the TRT. A comparison of wet and dry second-stage de-dusting of blast furnaces has been presented recently.

The aim of this study was to gain more detailed information on the separation of gaseous components in the top-gas scrubber of a blast furnace. The separation efficiency for various components was determined by simultaneous measurements upstream and downstream of the scrubber of an industrial blast furnace. These efficiencies were compared with the typical separation efficiencies which can be achieved in dry sorption gas cleaning processes.

2. Material and Methods

2.1. Description of the Blast Furnace

The measurements were performed at the top-gas scrubber of blast furnace A (BFA) at voestalpine in Linz. BFA is a pressurized blast furnace with a hearth diameter of 12.0 m. The top gas pressure at the furnace top is regulated to 2.3 bar (g). With a working volume of 3 125 m³ BFA reaches a maximum melting rate of 8 500 t/day of hot metal. The hot blast is injected via 32 tuyères with an average pressure of about 4 bar (g).

The blast furnace top gas is treated in a two-stage gas cleaning system: In the first stage (a dust catcher) the coarse fraction of the BF dust (about 60–80% of the total dust amount) is removed. The second stage consists of a wet scrubber (annular gap scrubber - system Bischoff) which decreases the final dust concentration to a level below 1 mg/m³ (STP). After the scrubber the blast furnace gas is expanded to the grid pressure via a top gas recovery turbine (TRT) with an electrical power generation of approximately 10 MW.

2.2. Off-gas Measurements

The off-gas samples were extracted upstream and downstream of the scrubber simultaneously. In total, five measurement series were performed. The measurements were performed according to VDI 4200. At each measuring point four sampling trains were used. Each sampling train consisted of a filter for removal of the dust particles and two subsequent gas washing bottles. In the first sampling train the absorption liquid was H₂O for separation of the acidic components HCl, HF and HBr (VDI 2470 Bl1; ÖNORM EN 1911). In the second sampling train 0.1 m NaOH was used for the separation of SO₂ and gaseous pollutants such as ammonia and hydrogen chloride are separated from the top-gas. A fourth sampling train with 3% H₂O₂ was used for the separation of SO₂ (ÖNORM EN 14791). Sampling time was 30 min. For the analysis of H₂S, COS, CS₂ and CH₃SH gas samples were collected into a Teflon bag.

HCl, HF and HBr were analyzed by ion chromatography according to VDI 2470 BI[19] and ÖNORM EN 1911. The analysis of SO₂ was done applying the Thorin-method according to ÖNORM EN 14791. For the analysis of NH₃ a photometric measurement was used according to ISO 15923-1 and HCN was analyzed according to DIN 38405-13. The components H₂S, COS, CS₂ and CH₃SH were analyzed by gas chromatography (DIN 51855-8).

2.3. Absorption of Components

In the scrubber, gaseous components can be absorbed in the scrubber water. The equilibrium of the absorption of a single component in pure water can be described by Henry’s law. In Eq. (1) Henry’s law is shown in a simplified form for diluted systems, assuming an activity coefficient in the liquid of 1.0:

\[ p_i = x_i \cdot H_i \]  \hspace{1em} (1)

where \( p_i \) is the partial pressure [bar] of the component in the gas phase and \( x_i \) is the mole fraction of the component in the liquid [−]. \( H_i \) is the Henry coefficient of the component [bar]. The higher \( H_i \) the less soluble is the component in water. In Table 1 the Henry coefficients are summarized for

| Component | \( H_i \) * in bar |
|-----------|------------------|
| HCl       | 0.1              |
| SO₂       | 45               |
| H₂S       | 640              |
| COS       | 2 600            |
| HCN       | 6.0              |
| NH₃       | 1.0              |

* Henry coefficients calculated from data reported by Sander
some investigated components.

However, the Henry coefficient gives only an indication about the solubility of a component in the scrubber water, because the solubility of a component in the scrubber water is influenced by the other components dissolved, e.g. the pH value of the scrubber water is below 7 because of the absorbed acid components.

2.4. Calculations for the Bjerrum Diagrams

In aqueous solutions gaseous components absorbed from the waste gas often react with water. For a highly acidic compound like hydrogen chloride this reaction results in a practically complete dissociation into protons and the corresponding anion. For compounds of medium or low acidity the dissociation in aqueous solution is not complete. Therefore, un-dissociated acid as well as the corresponding anions are present in the solution. Since the dissociation also produces protons and the dissociation reaction is an equilibrium reaction, the concentrations of un-dissociated acid and anion are strongly dependent on the pH-value of the aqueous solution. To visualize this dependence the Bjerrum diagram can be used. A Bjerrum diagram shows the concentrations or activities of the various ions of a component that can dissociate as a function of the pH value.

For the blast furnace off-gas components HCN and H2S the following equilibrium reactions have to be taken into account:

\[
\text{HCN}_{\text{aq}} \leftrightarrow \text{H}^+ + \text{CN}^- \quad \text{K(HCN)} \quad \text{(2)}
\]

\[
\text{H}_2\text{S}_{\text{aq}} \leftrightarrow \text{H}^+ + \text{HS}^- \quad \text{K(H}_2\text{S)} \quad \text{(3)}
\]

\[
\text{HS}^- \leftrightarrow \text{H}^+ + \text{S}^{2-} \quad \text{K(H}_2\text{S)} \quad \text{(4)}
\]

The numeric values for the compounds 1 to j at standard temperature R…gas constant (8.314 [J/(mol.K)])

A detailed description for the calculation can be found in the literature. Assuming constant heats of reaction \((\Delta H_{i,j}^0)\) the van’t Hoff equation was used for the adaption of the equilibrium constants to scrubber water temperature (Eq. (9)):

\[
\ln \left( K_i^T \right) = \ln \left( K_i^0 \right) + \frac{\Delta H_{i,j}^0}{R} \left( \frac{1}{298.15} - \frac{1}{T} \right) \quad \text{(9)}
\]

\(K_i^T\) …dimensionless thermodynamic equilibrium constant at temperature T [K]

\(\Delta H_{i,j}^0\) …heat of reaction at standard temperature for reaction i

The respective heats of reaction at standard temperature were calculated from the relevant heats of formation \((\Delta H_{i,j}^0)\) for the compounds used in Eqs. (7) and (10) were taken from the literature.

The assumption of constant heats of reaction over the temperature range of approximately 30 K (difference between scrubber operation temperature and standard temperature) standard temperature in the above equilibrium reactions is quite reasonable. For HCN the equilibrium constant was calculated for various temperatures under this assumption and was compared with published values. As shown in Fig. 2 the values calculated in this study correlate to a high extent with the published data; the correlation coefficient was 0.98.

The equilibrium constants resulting from the calculations are on a molality basis (mol/kg solvent) for infinite diluted
The conversion into concentration based equilibrium constants was carried out with the simplification of an activity coefficient of 1.0. The calculated equilibrium constants (given as pK-values, the negative decadic logarithm of the equilibrium constants) of the various reactions at 56°C (average scrubber water temperature) are summarized in Table 2.

The calculated equilibrium constants and the mass balance for the species involved were used for the calculation of the Bjerrum diagrams.

3. Results and Discussion

3.1. General Operation Data of the Scrubber

The volumetric top-gas flow was quite constant for all measurements (8 410 ± 40 m³ (STP)/min). The top-gas temperature before the scrubber varied between 99°C and 113°C and the temperature after the scrubber was constant at 56°C. The concentration of the main components only varied slightly. The concentrations of CO, CO₂ and H₂ were 23.6 ± 0.3% (vol), 22.7 ± 0.4% (vol) and 6.2 ± 0.3% (vol), respectively. The concentrations of CO and CO₂ were well within the data reported in the BAT Reference Document, while the concentration of H₂ was somewhat above the reported range.

Also the operation conditions at the scrubber were constant. The scrubber water flow was approximately 1 200 m³/h (without internal recycle) and the scrubber pressure drop 20.3 ± 0.3 kPa. The pH-value of the scrubber water was 5.6 ± 0.1. In the scrubber water the average concentration of CN⁻ at the scrubber outlet was 0.15 ± 0.02 mg/dm³ and the total content of dissolved sulphur was 55.5 ± 2.1 mg/dm³. The scrubber outlet flow is piped to the waste water treatment plant of the blast furnaces. For this reason the measured concentrations at the scrubber outlet are higher than the actual emission values of the blast furnace waste water.

3.2. Measured Concentrations of Gaseous Pollutants and Separation Efficiency

The concentrations of HF and HBr were below the detection limit (0.1 mg/m³ (STP)), with one exception, and the concentrations of CS₂ and CH₃SH were always below the detection limit (1.0 mg/m³ (STP)). The average concentrations of these other components measured are summarized in Table 3.

The concentration of H₂S measured was in the reported range of 14 mg/m³ (STP), whereas the concentration of HCl is substantially lower than the reported value of 0.26–1.0 mg/m³ (STP). However, the reported value refers to the sum of CN⁻ which also includes solid cyanide contained in the dust. According to the literature cyanide is present in the BF top gas mainly in the form of HCN, NaCN and KCN.

The emission of sulphur with the blast furnace gas is dominated by COS. This component accounts for approximately 85% of the sulphur of the total sulphur emissions in the gas after the scrubber of 176 mg/m³ (STP), while H₂S and SO₂ account only for 15% and 0.6%, respectively. The concentration of COS during the measuring campaign was approximately twice as high as the average concentration known from operational measurements. The reason for this observation is not clear. A measuring error can be excluded because operational measurements during the measuring campaign showed the same increased concentrations.

The separation efficiency for HCl was high. Significant separation was observed also for SO₂ and NH₃. Absorption of these components has to be expected because of their low Henry coefficient (Table 1).

For the weak acids H₂S and HCN the separation efficiency was negative because the concentration of these components was higher in the gas after the scrubber than before the scrubber. In contrast to HCN, which has a low Henry coefficient, the high Henry coefficient of H₂S does not favour absorption. However, this cannot explain an increase of the concentrations of these components. Bjerrum plots can help to understand the phenomenon. Dissolved H₂S dissociates in water according to the Eqs. (3) and (4). A Bjerrum plot shows the concentrations of the various species as a function of the pH value (Fig. 3, left). At the pH-value of the scrubber water of 5.6 the dissociation of H₂S to HS⁻ is minimal. Thus, equilibrium is very much on the side of physically dissolved H₂S in the scrubber water. The dust separated in the scrubber also contains some sulphides and cyanides. These sulphides and cyanides of alkali metals are dissolved in the scrubber water due to their high solubility in water. For example the solubilities (in g solute/100 g of water) of Na₂S, NaCN and KCN are 36.4 (50°C), 82 (35°C) and 69.9 (20°C) respectively.

Under the conditions of the investigation the dissolution reactions

\[ \text{Na}_2\text{S} \rightarrow 2 \text{Na}^+ + \text{S}^{2-} \] ........................ (11)

\[ \text{NaCN} \rightarrow \text{Na}^+ + \text{CN}^- \] .......................... (12)

can be regarded as being completely on the product (S²⁻).

### Table 2. Equilibrium constants (pK) at 56°C.

| Gas component | reaction | pK |
|---------------|----------|----|
| HCN           | (2)      | 8.52 |
| H₂S           | (3)      | 6.63 |
|               | (4)      | 12.09 |
| SO₂           | (5)      | 2.06 |
|               | (6)      | 7.38 |

### Table 3. Concentrations of various components in BF top gas.

| Gas component | Average concentration before scrubber* | Average concentration after scrubber* | Average separation efficiency |
|---------------|----------------------------------------|---------------------------------------|-----------------------------|
|               | mg/m³ (STP)                            | mg/m³ (STP)                           | %                           |
| HCl           | 5.8 ± 3.3                               | 0.26 ± 0.10                           | 96                          |
| SO₂           | 11.9 ± 3.3                              | 2.2 ± 0.6                             | 81                          |
| H₂S           | 7.6 ± 8.6                               | 28.0 ± 15.7                           | −270                        |
| COS           | 264 ± 9                                 | 279 ± 5                               | −6                          |
| HCN           | 0.07 ± 0.06                             | 0.12 ± 0.06                           | −66                         |
| NH₃           | 0.28 ± 0.14                             | 0.15 ± 0.04                           | 46                          |

* average concentration ± standard deviation
The increase of the $S^{2-}$-concentration in the scrubber due to the introduction of the dust pushes the equilibrium reactions (3) and (4) to the left side forming un-dissociated $H_2S$ according to the actual pH-value. When the maximum solubility of $H_2S$ is exceeded $H_2S$ is released into the gas phase. A similar effect can take place with $HCN$. Dissolved $HCN$ dissociates in water according to Eq. (2). The middle of Fig. 3 shows the Bjerrum plot for cyanide species as a function of the pH value. The pH-value of the scrubber water is small. The dust separated in the scrubber also contains some water soluble $KCN$ and $NaCN$. These cyanides get completely dissolved in the scrubber water shifting the equilibrium reaction (2) to the side of un-dissociated $HCN$. This $HCN$ is released to the gas phase when the maximum solubility of $HCN$ is exceeded. A similar effect has been described recently. It was observed that at the sedimentation unit of a blast furnace scrubber water system dissolved cyanides are released into the atmosphere as $HCN$.

The Bjerrum plot for $SO_2$ (Fig. 3, right) shows that the formed $H_2SO_3$ dissociates at the pH-value of the scrubber water and the dominating species is $HSO_3^-$. Thus, the absorption of $SO_2$ is promoted.

The COS concentrations at the scrubber inlet and the scrubber outlet were nearly identical, no absorption was observed. This observation is supported by the high Henry coefficient of COS (Table 1).

### 3.3 Comparison with a Dry Sorption System

The average separation efficiency of the scrubber of 96% for the strong acid $HCl$ is quite high. This is beneficial for the downstream gas duct and the TRT because $HCl$ is the main cause of corrosion in this area. In a dry second dedusting stage acid gases are not separated. Nevertheless, separation of acid gases can be achieved by an integrated dry sorption process using hydrated lime or sodium bicarbonate as sorbent. With such dry sorption systems a similar separation efficiency for $HCl$ can be achieved. However, published results are from applications with a considerably higher $HCl$ inlet concentration. Therefore, experiments have to verify that the high separation efficiency can also be achieved at lower inlet concentrations.

The separation efficiency for $SO_2$ was also high. By applying dry sorption systems a similar separation is possible, but the separation efficiency has to be proofed for the low concentrations present in the BF gas. Due to the low fraction of $SO_2$ on the total sulphur emission, which is dominated by COS, the separation efficiency for $SO_2$ might be less important.

The emissions of the weak acids $H_2S$ and $HCN$ would be less after a dry sorption process because the release of these components from their salts is not likely in such systems. The separation efficiency of the scrubber system for $NH_3$ was 46%. In a dry sorption system using base chemicals as sorbents $NH_3$ is not separated from the gas. Separation of $NH_3$ cannot be achieved by addition of base components. However, $NH_3$ can be separated when, for example, activated carbon is used as additional sorbent.

### 4. Conclusions

In this study the separation efficiency of gaseous components in the top-gas scrubber of a blast furnace was investigated. The concentrations of $HCl$, $HF$, $HBr$, $H_2S$, $SO_2$, $CO_2$, $H_2$ and $CH_4$ were measured in the off-gas before and after the scrubber system. The composition of the blast furnace top-gas ($CO_2$, $CO$ and $H_2$) and the operation conditions of the scrubber - volumetric top-gas flow, gas temperature, scrubber water flow, scrubber pressure drop and pH-value of the scrubber water - were very constant for all five measuring series.

From the hydrogen halides only $HCl$ was found in the gas. The concentrations of $HF$ and $HBr$ were nearly always below the detection limit.

The emission of sulphur with the blast furnace gas of 176 mg/m³ (STP) is dominated by COS which accounts for approximately 85% of the total sulphur emissions in the gas after the scrubber, while $H_2S$ and $SO_2$ account only for 15% and 0.6%, respectively. The concentrations of $CS_2$ and $CH_4$ were nearly always below the detection limit.

The concentrations of the nitrogen containing components $NH_3$ and $HCN$ were significantly lower than 1.0 mg/m³ (STP).

The average separation efficiency for the strong acidic component $HCl$ was 96%. Because of the pH-value of the scrubber water of 5.6 the average separation efficiency for
the weaker acidic SO₂ was reduced to 81%. The weak acids HCN and H₂S were not separated at all. In contrast, the concentration of these components was higher in the off-gas after the scrubber compared to the concentration before the scrubber. This phenomenon can be explained using the Bjerrum plots showing the dissociation equilibria of the various species as a function of the pH value. Dissolved sulphides and cyanides originating from the separated dust form un-dissociated H₂S and HCN which is released from the scrubber water to the gas.

The separation efficiency for NH₃ was 46%. COS was not separated in the scrubber system at all. This finding is supported by the high Henry coefficient for this component.

The measured separation efficiencies of the scrubber system might be achieved also by dry sorption gas cleaning processes. However, the efficiency of these processes at the fairly low over-all concentrations of the pollutants has to be proofed in experiments. In the case of a dry gas cleaning system, the concentrations of the weak acids H₂S and HCN in the clean gas would be even less.

Acknowledgement

The financial support of K1-MET is acknowledged. K1-MET is a member of COMET – Competence Centers for Excellent Technologies and is financially supported by the BMVIT (Federal Ministry for Transport, Innovation and Technology), BMWFW (Federal Ministry of Economy, Family and Youth), the federal states of Upper Austria, Styria and Tyrol, SFG and Tiroler Zukunftsstiftung. COMET is managed by FFG (Austrian research promotion agency).

Proofreading by S. Falkensammer is gratefully acknowledged.

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