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Oxygen Removal during Biogas Upgrading using iron-based Adsorbents

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ABSTRACT

In this study a new process for the combined removal of hydrogen sulfide and oxygen from biogas on iron-based adsorbents is described. Several commercial available iron oxides were tested in a screening. Detailed investigations on break-through behavior were carried out with the most promising adsorbent. The results of the experimental investigations verify the basic suitability of the procedure for oxygen removal below 10 vppm. Optimum process parameters, within the experimental range, have been quantified. A significant H_2S-loading of the adsorbent is required for sufficient subsequent oxygen removal. Temperature is the most important influential parameter on break-through curve, since a certain activation energy is required ($T > 80$ °C). As chemical reaction is the rate-determining step, residence time in fixed bed should be high enough. A relative gas humidity of about 15 % is also necessary.

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1 INTRODUCTION

One of the major issues of the energy industry is the integration of renewable energy sources into the energy supply system, together with the existing fuels. A technologically appropriate and important component of energy politics to mitigate the problem is feeding biomethane into the natural gas grid and its subsequent storage. In addition to the desulfurization and carbon capture during biogas purification, demands for oxygen removal coming up, especially from operators of natural gas grids or underground gas storage operators, to prevent corrosion respectively geochemical reactions. In the gas infrastructure, the negative influence of oxygen is eminently noticeable. Even at low levels of oxygen corrosion phenomena and the formation of elemental sulfur in pore and aquifer gas storages are determined [1, 2].

Therefore in most European technical regulations for underground gas storages and the European gas trade the oxygen content is limited to 10 vppm [3].

Currently existing techniques for oxygen removal – mainly based on noble metal catalysts – are currently very expensive in investment and operation. As a result of the research activities at DBI - Gastechnologisches Institut gGmbH Freiberg a process for the combined desulfurization and oxygen removal from biogas was developed [4, 5]. This technology uses iron-based adsorbents, henceforth referred as iron oxides. For this purpose detailed studies of the basic reaction mechanisms were made. The whole process has been optimized for different process parameters (especially: superficial gas velocity, H_2S and O_2 concentration, relative gas humidity, temperature). The aim was to determine the optimal composition of the iron oxides as well as the process sequence.

The advantages of this process are low investment and operating costs (process scheme, low-cost adsorbents, low temperatures, atmospheric pressure, etc.).

Oxygen requirements and resulting problems

The composition of natural gas, which is transported and traded Europe-wide, is regulated by EASEE-gas (European Association for the Streamlining of Energy Exchange - gas) in CBP 2005-001/02 (Common Business Practice) [3]. The maximum limit for the amount of oxygen in high pressure systems of the gas infrastructure is fixed to 10 vppm.

As part of the revision DVGW (German Technical and Scientific Association for Gas and Water) worksheet G 260 - *gas quality* in 2013, the oxygen limit has been adapted to EASEE-gas directive for high-pressure gas grids [6].

However, this limit can be seen as a compromise, since a previous pan-European measurement campaign in 2005, whereby the oxygen content of the natural gas in high pressure systems was less than 1 vppm in average [1, 7].

Thus, for example, in pipeline inspections of Gassco/Statoil considerable corrosion damage due to low concentrations of H_2S, O_2 and H_2O were found, whereupon the oxygen content was limited to 2 vppm [1].

Especially in moist areas of the gas infrastructure, the negative influence of oxygen is eminently noticeable. Corrosion phenomena and the formation of elemental sulfur (see Figure 1) in pore and aquifer gas storage are consequence even at low concentrations of hydrogen sulfide and oxygen [1]:

$$2\,H_2S + O_2 \rightarrow \tfrac{1}{4}\,S_8 + 2\,H_2O \qquad (1)$$

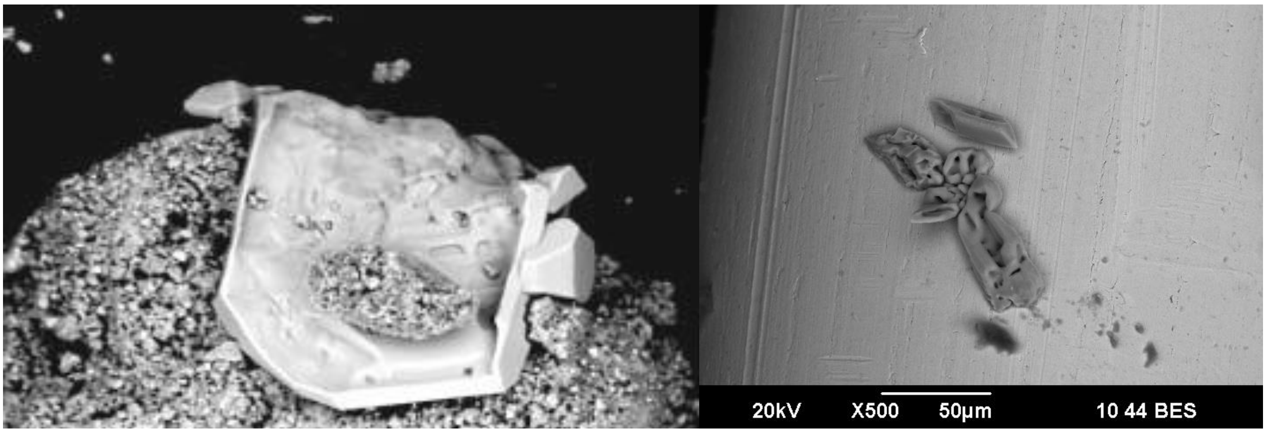
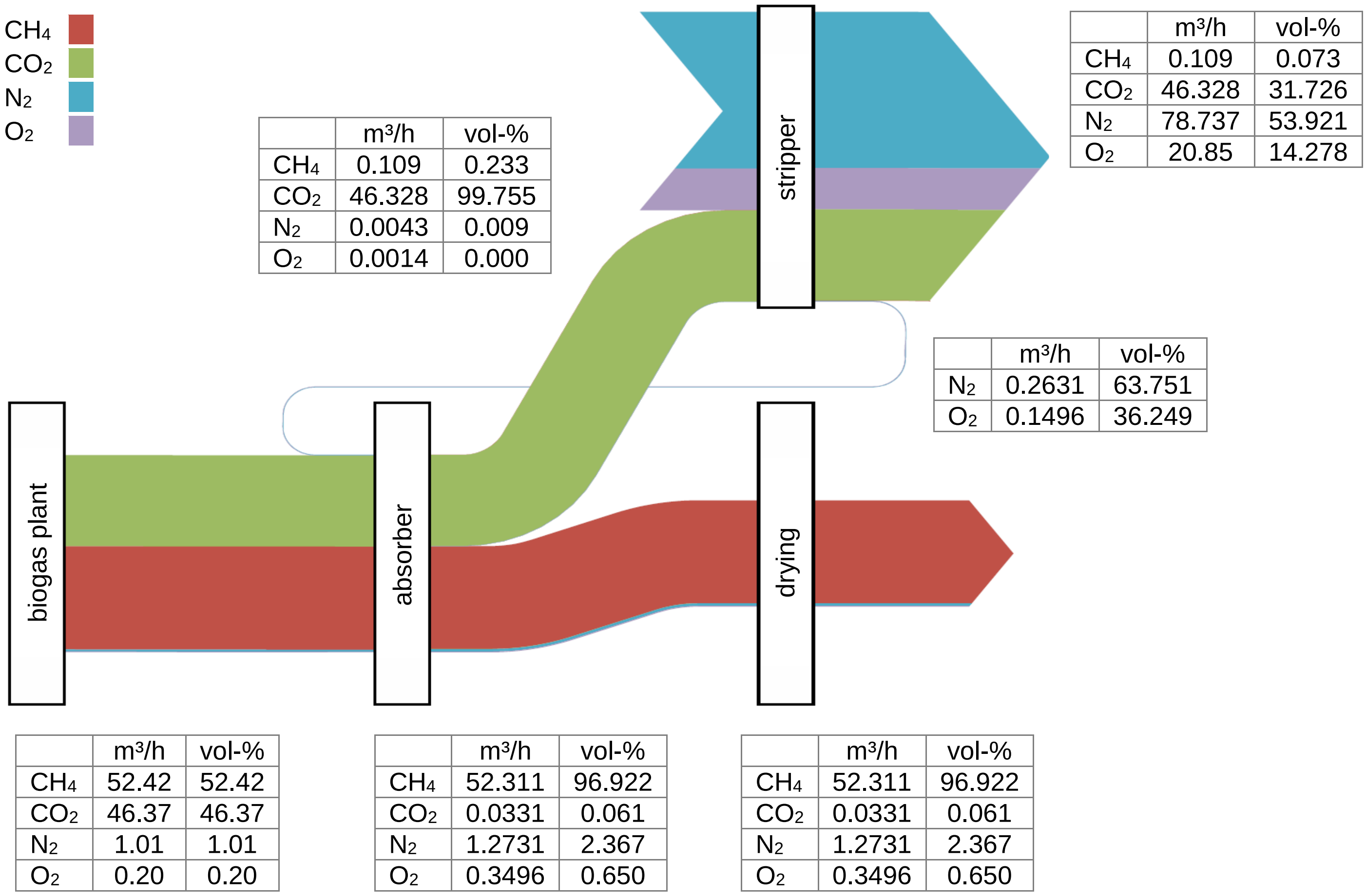


Figure 1: Rhomboidal sulfur crystals in gas pipeline on corrosion products (left) and stainless steel (right) [1, 8]

Oxygen contamination and removal

Entry of oxygen into the raw biogas on the substrate feed to digester is unavoidable. Even at subsequent gas treatment processes oxygen contamination can be expected. So in the desorber pressure water or Genosorb® scrubber small amounts of oxygen are dissolved in the washing liquid, succeeded back to the absorber and thus to pure gas (biomethane).

An example therefore is shown in the following sankey diagram of the biomethane-process chain via pressure water scrubbing (Figure 2).



	m³/h	vol-%
CH_4	0.109	0.073
CO_2	46.328	31.726
N_2	78.737	53.921
O_2	20.85	14.278

	m³/h	vol-%
CH_4	0.109	0.233
CO_2	46.328	99.755
N_2	0.0043	0.009
O_2	0.0014	0.000

	m³/h	vol-%
N_2	0.2631	63.751
O_2	0.1496	36.249

	m³/h	vol-%
CH_4	52.42	52.42
CO_2	46.37	46.37
N_2	1.01	1.01
O_2	0.20	0.20

	m³/h	vol-%
CH_4	52.311	96.922
CO_2	0.0331	0.061
N_2	1.2731	2.367
O_2	0.3496	0.650

	m³/h	vol-%
CH_4	52.311	96.922
CO_2	0.0331	0.061
N_2	1.2731	2.367
O_2	0.3496	0.650

Figure 2: Sankey diagram of O_2 contamination during pressure water scrubbing (ChemCad model) [4]

In recent biogas monitoring programs oxygen contents in range of 0.03 up to 0.8 vol-%, with an average content of 0.5 vol-%, have been reported [9, 10].

The possibilities of oxygen scavenging have been discussed extensively in the literature [11, 12]. A basic classification can be done in physical and chemical processes. A more detailed breakdown is shown in the following Table 1.

Table 1: Classification of methods for oxygen removal [11, 12]

physical processes	chemical processes
adsorption e.g. on mole sieves, active carbon	**chemisorption** on transition- or alkaline earth metals (e.g. copper); on sulfid iron oxides
membrane-process porous or solution-diffusion membranes	**absorption** pyrogallol, chromium(II) chloride, hydrazine, sodium sulfite, i ganic oxygen scavengers in the form of $ABC_4O_{7+\delta}$ (A = rare metal, B = Ba, C = Co) [13]
cryogenic separation condensation or rectification	**catalytic oxidation** H_2, CH_4, higher hydrocarbons

The methods of methane oxidation and chemisorption on sulfidized iron oxides offer the highest potential from a technical and economic point of view.

The sections below deal with the chemisorption on sulfidized iron oxides in more detail.

2 PROCESS OF OXYGEN CHEMISORPTION ON SULFIDIZED IRON OXIDES

In this study a new process for simultaneous removal of hydrogen sulfide and oxygen on iron-based adsorbents is described. In the first step the desulfurization based on chemisorption of H_2S on iron oxides is carried out in a fixed bed [14–17]:

$$Fe_2O_3 + 3\ H_2S \rightarrow Fe_2S_3 + 3\ H_2O \quad (2)$$

$$2\ Fe(OH)_3 + 3\ H_2S \rightarrow Fe_2S_3 + 6\ H_2O \quad (3)$$

The second step is the regeneration with oxygen-laden biogas:

$$Fe_2S_3 + 3/2\ O_2 \rightarrow Fe_2O_3 + 3/8\ S_8 \quad (4)$$

$$Fe_2S_3 + 3/2\ O_2 + 3\ H_2O \rightarrow 2\ Fe(OH)_3 + 3/8\ S_8 \quad (5)$$

where elemental sulfur and iron oxides are formed (Figure 3). (Note that the reactions are much more complex and involve several intermediate species.)

A possible technical implementation of the system is schematically shown in Figure 3. Thereby two connected fixed bed reactors are integrated in a biogas purification plant, which are in alternate operation (desulfurization/deoxygenation). In the first reactor the desulfurization is carried out (eq. (2), (3)). After that CO_2 is separated and the biogas is upgraded to natural gas standards with further processing steps. The oxygen-laden biomethane reaches the second reactor, which was treated with hydrogen sulfide in a previous cycle. In this step the removal of oxygen by reaction with sulfidized iron oxides takes place (eq. (4), (5)). This reactor is used for desulfurization in the next cycle.

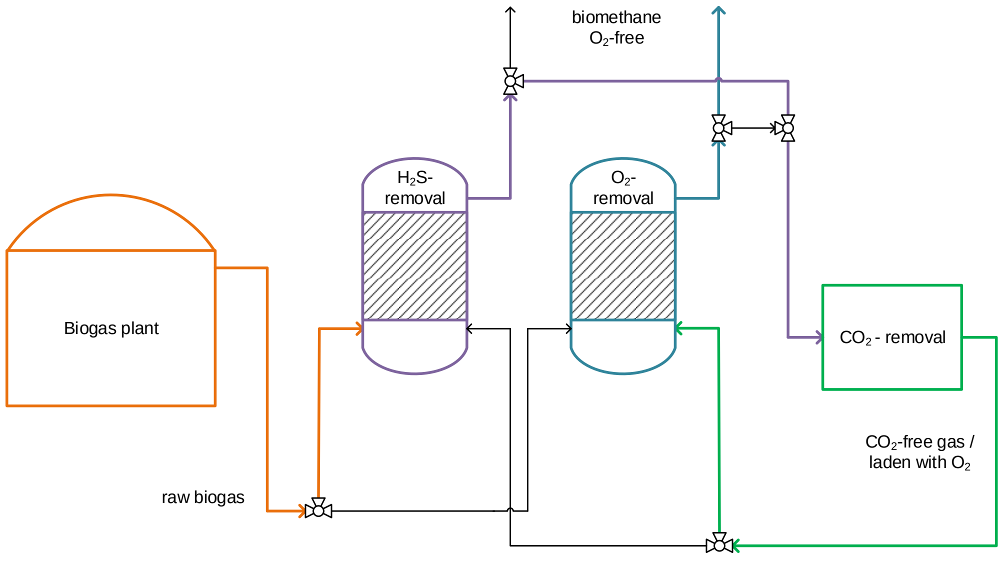


Figure 3: Simultaneous removal of H_2S and O_2 during biogas purification process [4]

3 EXPERIMENTAL INVESTIGATION

Methodology

To investigate this process in detail, following studies were carried out:

- measurement of break-through curves for hydrogen sulfide and oxygen,
- characterization of adsorbents towards grain-size distribution, porosity, specific surface, XRD and DSC,
- determination of the optimal process parameters for scale-up, e.g. hydrogen sulfide and oxygen concentration, gas velocity, relative gas humidity, temperature,
- mathematical modeling of the process.

Testing and results

In literature the ratio between outlet and inlet concentration, for example $c/c_0 = 0.05$, is described and in these studies also considered [18]. The time to reach the break-through criterion is called break-through time t_{DB}. The general equation of the mass-based loading at time t:

$$X_i(t) = \frac{\dot{V}_i \cdot c_{i,0}}{m_{Ads}} \cdot \int_0^t \left(1 - \frac{c_i(t)}{c_{i,0}}\right) \cdot \mathrm{d}t \qquad (6)$$

results in break-through loading X_{DB} with break-through time t_{DB} (approximately ideal break-through curve – S-shape):

$$X_{DB,i} = \frac{p \cdot \dot{V}_i \cdot t_{DB} \cdot c_{i,0} \cdot M_i}{R_m \cdot T \cdot m_{Ads}} \qquad (7)$$

Both are important criteria for the regulation and control of fixed bed adsorbers.

To determine the experimental plan following process parameters are considered:

- superficial gas velocity,
- inlet oxygen concentration,
- relative gas humidity,
- temperature.

The following figures present the results of experimental investigations on break-through behavior of sulfidized iron oxides towards oxygen. Therefore the combination of two influence parameters is shown, the other remain in the basic system accordingly.

Figure 4 shows the break-through loading $X_{DB,O2}$ over superficial gas velocity and inlet concentration of oxygen.

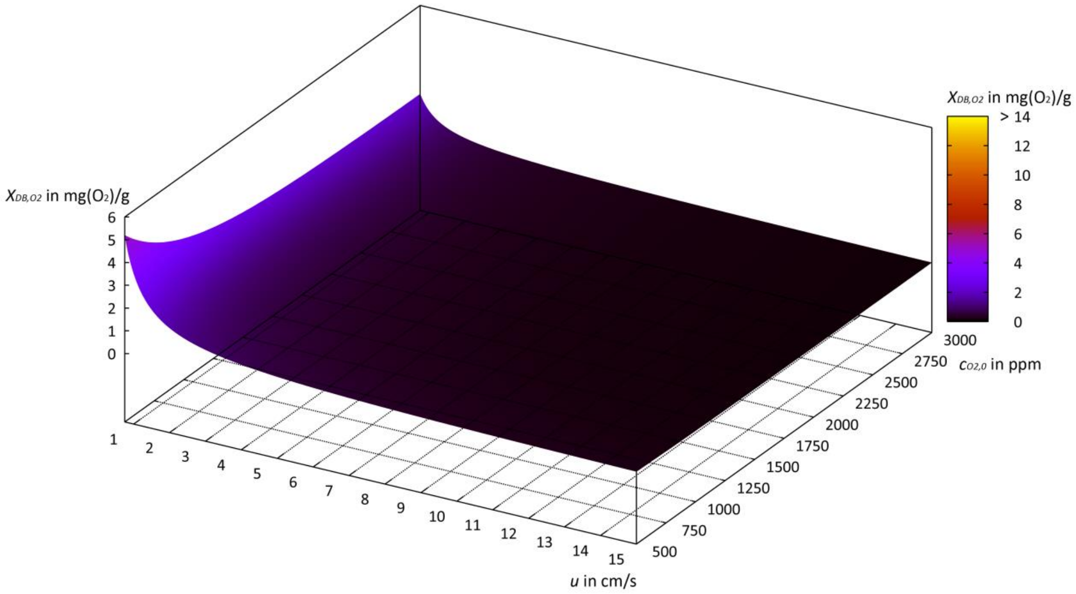


Figure 4: *Break-through loading of oxygen $X_{DB,O2}$ on sulfidized iron oxide over superficial gas velocity u and inlet concentration of oxygen $c_{O2,0}$ [4]*

Figure 4 illustrates that at low superficial gas velocities and low input concentrations, the highest break-through loadings are achieved. The theoretical maximum of $X_{DB,O2}$ = 5.20 mg(O_2)/g is reached for a velocity of 0.75 cm/s and an initial concentration of 500 vppm(O_2).

Figure 5 shows the break-through loading $X_{DB,O2}$ over inlet concentration of oxygen and temperature.

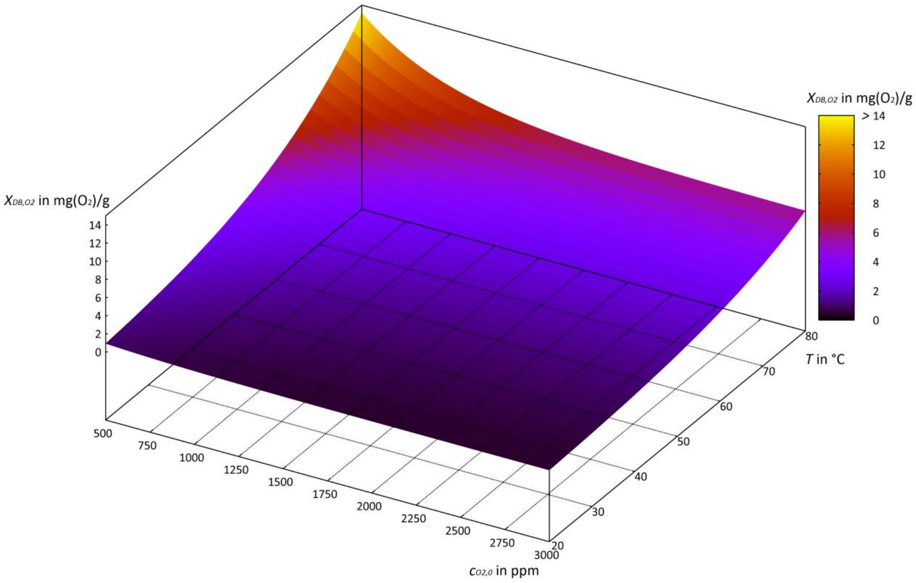


Figure 5: *Break-through loading of oxygen $X_{DB,O2}$ on sulfidized iron oxide over inlet concentration of oxygen $c_{O2,0}$ and temperature T [4]*

The highest loading is to be expected at low input concentrations and high temperatures. The theoretical maximum value in combining the two influencing variables is $X_{DB,O2}$ = 14.13 mg(O_2)/g for an input concentration of 500 vppm(O_2) and a temperature of 80 °C.

Figure 6 shows the break-through loading $X_{DB,O2}$ over relative gas humidity and temperature.

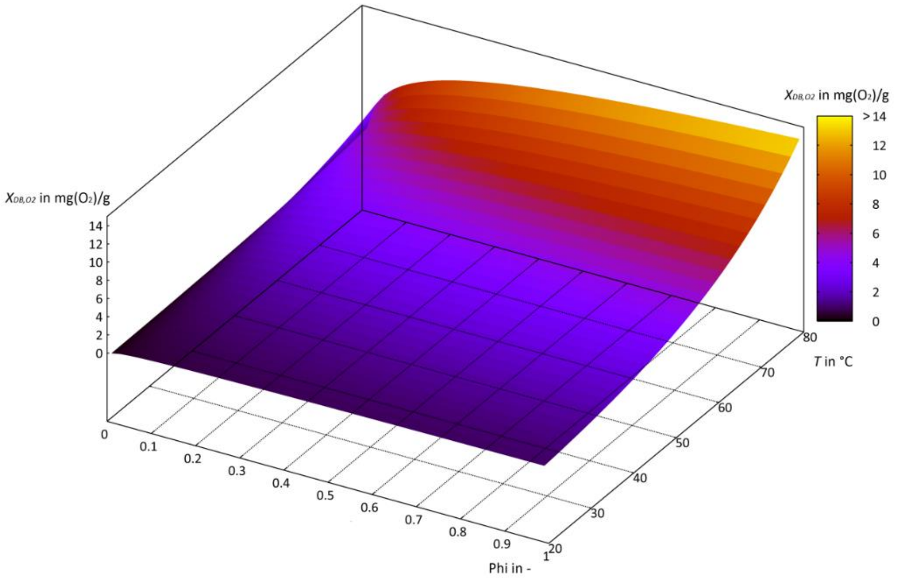


Figure 6: *Break-through loading of oxygen $X_{DB,O2}$ on sulfidized iron oxide over relative gas humidity φ and temperature T [4]*

Figure 6 illustrates that the break-through loading decreases strongly with decreasing relative gas humidity independently of temperature. This effect can be observed from approximately 15 %. The reason could be found in the stoichiometry of oxygen removal, as water is required for the reaction (eq. (5)). The highest loading is expected for saturated gases at high temperatures. The calculated maximum of the break-through loading is $X_{DB,O2}$ = 13.59 mg(O_2)/g for 80 °C and saturated gas.

Figure 7 shows the break-through loading $X_{DB,O2}$ over superficial gas velocity and temperature.

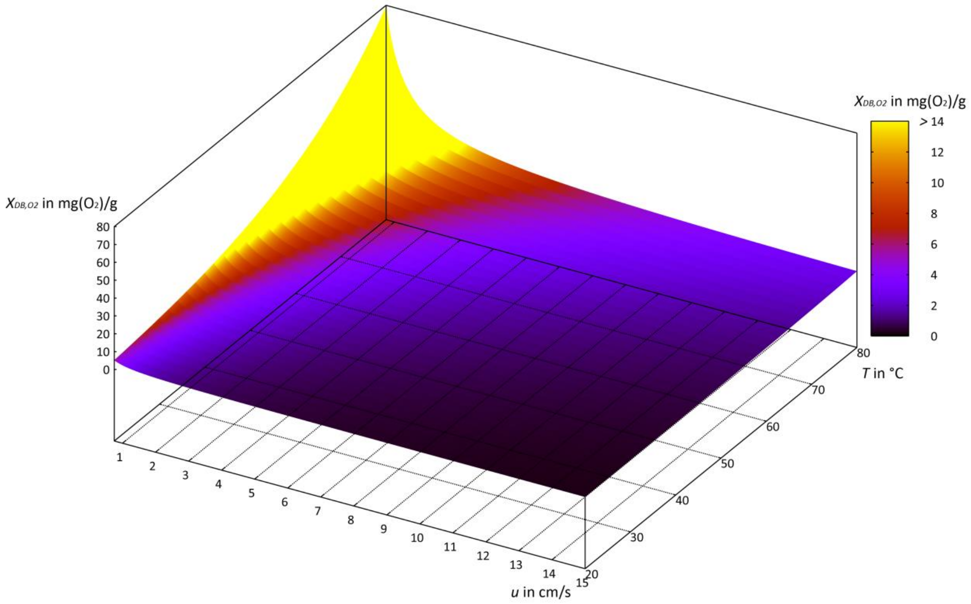


Figure 7: *Break-through loading of oxygen* $X_{DB,O2}$ *on sulfidized iron oxide over superficial gas velocity u and temperature T [4]*

This introduces high break-through loadings at low superficial gas velocities and high temperatures. The theoretical maximum of $X_{DB,O2}$ = 79.56 mg(O_2)/g represents a flow velocity of 0.75 cm/s and a temperature of 80 °C. This value can be obtained only when the appropriate loading is guaranteed with hydrogen sulfide.

Discussion

In summary, the following statements concerning the influence of parameters on the break-through loading can be made:

- significant loading of the adsorbent with hydrogen sulfide is required for efficient oxygen removal
- temperature is the most important influential parameter on break-through curve (activation energy)
- residence time in fixed bed should be high (chemical reaction rate-determining step, eq. (4), (5))
- relative gas humidity of about 15 % is necessary (consumption during regeneration, eq. (5))

In Table 2 a summary of die experimental results is given.

Table 2: Parameter and influence on break-through loading of oxygen on sulfidizied iron oxide [4]

parameter	**influence on $X_{DB,C}$**	**optimum (within experimental range)**
u	↑	< 1 cm/s
$c_{O2,0}$	→	preferably low (500 vppm), process-dependent
φ	→	saturated, however min. moisture > 15 %
T	↑↑	> 80 °C
influence factor: ↑↑ - very high, ↑ - high, → - low		

4 SUMMARY AND OUTLOOK

The results of the experimental investigations verify the basic suitability of the procedure for oxygen removal below 10 vppm (EASEE-gas [3]). Also the optimal process parameters, within the experimental range, were identified.

Problem of this procedure is, that there is usually a higher O_2-concentration in biomethane than stoichiometrically with H_2S-content in raw gas removable (see eq. (1)). However, in future there will be an increase of the amount of domestic and industrial waste in substrate and thus H_2S-content too, especially in Germany. A current useful application of the combined process of desulfurization and oxygen removal on iron oxides is the integration in biogas purification plants with pressure swing adsorption or amine scrubber.

Despite the promising potential of the process on present stage, the used adsorbents, which are designed for desulfurization, are not yet efficient for O_2 conversion. Thus, the optimization of the sorbent for the simultaneous removal of O_2 and H_2S is currently under investigation, using a knowledge based approach, which implies studies of reaction mechanism as well as structure-activity correlation.

5 SYMBOLS AND ABBREVIATIONS

c	concentration in mg/m³ or vol-%
φ	relative gas humidity in %
T	temperature in °C
u	superficial gas velocity in m/s
X	loading in mg/g

0	inlet, start

CBP	Common Business Practice
DB	ger.: Durchbruch, break-through
DSC	differential scanning calorimetry
DVGW	German Technical and Scientific Association for Gas and Water
EASEE-gas	European Association for the Streamlining of Energy Exchange - gas
XRD	X-ray diffraction

6 LIST OF REFERENCES

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7 LIST OF FIGURES

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