Impact of highly concentrated contaminants on the quality of oxygen 93 % produced by pressure swing adsorption

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ABSTRACT

A zeolite based pressure swing adsorption (PSA) module designed to produce medicinal oxygen with 90 – 96 % oxygen content was exposed to high input concentrations and high total amounts of CO (17.7 %, 44 mol), CO_2 (16.5 %, 23 mol), NO_2 (0.98 %, 2 mol), NO (6.2 %, 6 mol) and SO_2 (4.2 %, 6 mol). In addition the system was operated with up to 35 % argon in the feed gas.

An empirical model was developed to describe the dependence of the oxygen concentration in the product on the oxygen concentration in the input. If the oxygen concentration in the feed gas was reduced below 18 % by dilution, the oxygen concentration in the product fell under the 90 % threshold.

Additional effects were observed with NO, NO_2 and SO_2 which are apparently due to chemical reactions on the adsorbent. These effects consisted of a further decrease in the oxygen concentration measured in the product and could not be reversed by excessive regeneration of the module with air.

Under the experimental conditions used, only CO was detected in the product. Appropriate CO monitoring of the input gas is considered a possible remedy for PSA modules in order to ascertain the pharmaceutical quality of the oxygen produced.

KEYWORDS

Pressure swing adsorption, medicinal oxygen, contamination monitoring, adsorption performance of zeolite A.

1. INTRODUCTION

Oxygen 93 % [1] is produced in single-stage concentrators by continuous PSA purification of ambient air [2] using zeolites [3]. The product gas must comply with specific requirements in terms of the contaminants CO_2, CO, NO, NO_2 and SO_2 among others.

PSA can be thought of as a chromatographic procedure with periodically changing flow direction so that gases with different retention properties are separated. The break through capacity of which depends primarily on the concentration of a constituent in the feed gas [4]. Little information is available in the scientific literature on the behaviour of zeolite based concentrators when exposed to high concentrations (more than 1 %) of CO_2, CO, NO, NO_2 and SO_2 in the air used.

The continuous production of oxygen 93 % requires continuous monitoring of the resulting gas to ascertain its pharmaceutical quality. The main objective of this work was to assess whether measurement of oxygen alone is sufficient to establish the required purity and content.

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A secondary aim was to investigate whether the interaction of these contaminants with the zeolite results in lasting changes in the performance of the concentrator.

Furthermore we intended to establish principles for the development of future standardised test procedures for PSA modules.

2. MATERIALS AND METHODS

All experiments were carried out with an oxygen concentrator module (Stephan Medizintechnik, Gackenbach, Germany).

The module consisted of 12 columns arranged in a parallel design and contained a total of 3 kg zeolite A.

All experiments were carried out in the quality assurance laboratories of basi Schöberl in Rastatt, Germany.
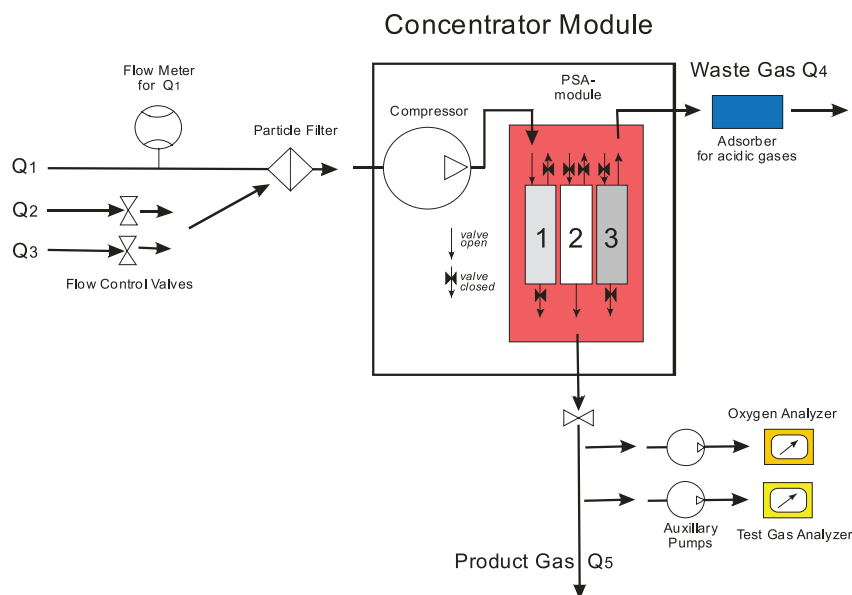
The design of the laboratory setup is shown in Figure.1:

Figure 1 – *Block diagram of experimental setup:*
Q1 = ambient air flow, Q2 = contaminant gas flow, Q3 = additional oxygen flow,
Q4 = waste gas flow, Q5 = product gas flow. Three of twelve columns in
the PSA-module are shown in the diagram representing; 1. loading phase,
2. discharge of O₂/Ar as product gas, 3. venting of remainder into waste gas.

Defined flow rates were set for ambient air (Q_1), contaminant (Q_2), additional oxygen (Q_3) and product gas (Q_5). Product gas flow (Q_5) was fixed by means of a flow control valve to 10 L/min as recommended by the manufacturer. The total input flow was always 127 ± 2 L/min as delivered by the internal compressor of the module. Q_2 and Q_3 were set to predetermined values from the local gas supply. The resulting flow of ambient air (Q_1) was then measured with a hot wire anemometer (TSI 4000, Driesen+Kern, Bad Bramstedt, Germany). For example, a flow of 10 L/min of N_2 was achieved by adjusting the N_2 valve so that a Q_1 of 117 L/min was registered, (127-117 = 10 L/min), see also Table 1.

Gas for analysis was pressureless sampled from the product gas flow. The oxygen measurements were carried out with a paramagnetic oxygen analyzer (OA 570A, Servomex, Ratingen, Germany).

The gas for the analysis of CO_2, CO, NO, NO_2 and SO_2 was transported with a membrane pump (KNF, Freiburg, Germany).

The following analyzers were used:

- CO_2/CO IR spectrophotometer (NGA 2000, Rosemount, South Africa); precision ± 10 %, detection limit CO about 1 ppm, CO_2 about 5 ppm,
- NO/NO_2 Chemoluminescence (CLD 700 EL, eco physics, Munich, Germany); precision ± 3 %, detection limit about 0.2 ppm,
- SO_2 FTIR spectrophotometer (Gasmet, Ansyco, Karlsruhe, Germany); precision ± 2 %, detection limit about 5 ppm.

The main constituent of the feed gas was always ambient air (Q_1).

All other gases used in the experiments were supplied by basi and were 99.9 % pure or better. N_2, Ar, CO_2 and O_2 were directly taken from the central gas supply.

CO was available as a mixture of 29.9 % in synthetic air stored in a 50 L cylinder at 150 bar.

NO_2 was available as a mixture of 9.8 % in synthetic air stored in 50 L cylinder at 10 bar. Higher concentrations or higher pressure were not feasible without phase separation.

NO was available as a mixture of 12.9 % in N_2 stored in a 50 L cylinder at 65 bar. N_2 was used as a carrier for NO in order to prevent the *in situ* formation of NO_2. Higher concentrations or higher pressures were not feasible without phase separation. The oxygen concentration of the feed gas was adjusted if required by addition of oxygen (Q_3).

SO_2 was available as a mixture of 10.0 % in synthetic air in a 50 L cylinder at 30 bar. Higher concentrations or higher pressure were not feasible without phase separation.

The achievable oxygen concentration in the product gas depends on the product gas flow and within a small margin on the oxygen concentration in the feed gas [5]. The experiments were designed to vary the oxygen concentration at constant product flow as compiled in Table 1.

Table 1 – *Experimental conditions: gas flow*

	Q_2 [L/min]	Q_3 [L/min]	Number of experiments
N_2	5 - 25		6
Ar	4 - 44		4
CO_2	5 - 21		5
O_2		5 - 15	4
CO	5 - 75		6
NO_2	12.5		1
NO*	33	7	4
SO_2	13 - 52		4

Q_2 and Q_3 were calculated as the difference between the total input flow and the reading of Q_1.

* Q_3 was adjusted 1st and then kept constant.

3. RESULTS

3.1 Effect of the contaminants on the oxygen concentration in the product gas

The measured oxygen concentration in the product gas showed systematic fluctuations within a period of 28 seconds. Therefore in all measurements minimum and maximum values within the period were documented. The differences between minimum and maximum increased with decreasing oxygen concentration in the feed gas and amounted to typically between 1 % and 2 % in the product gas.
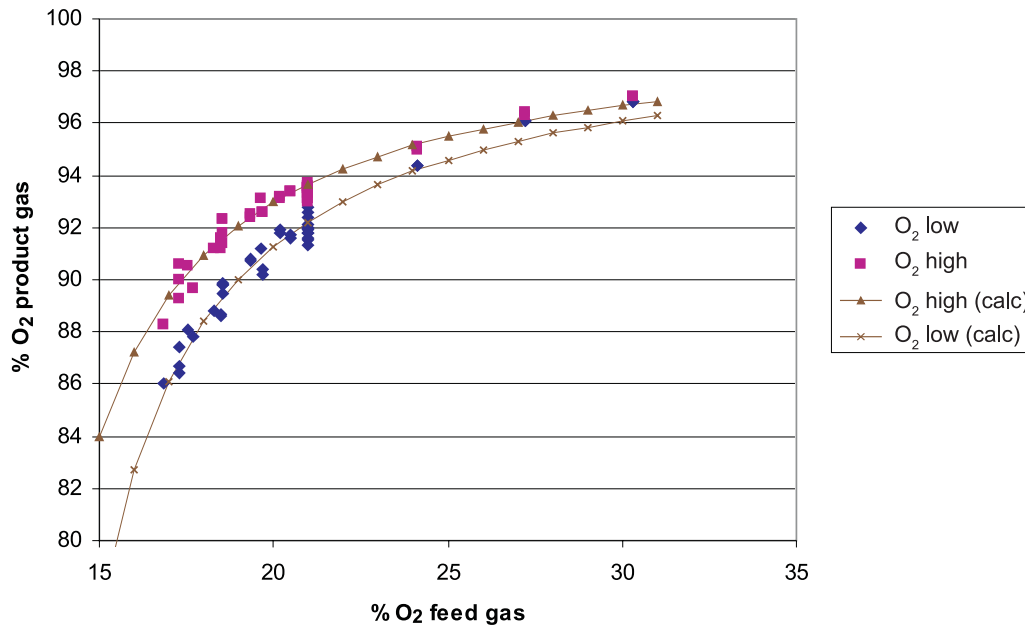

Figure 2 –   *Dilution effect of N_2, O_2, CO_2 and CO on the O_2 output concentration.*
O_2 low, O_2 high: observed oxygen concentrations.
O_2 high (calc) and O_2 low (calc) were calculated using Equation. 1 (see text).

In Figure 2 the oxygen concentration in the product gas is depicted as a function of the oxygen concentration in the feed gas for added N_2, O_2, CO_2 and CO.

These gases showed a common pattern which could be described by an empirical relationship:

$$O_2 (calc) = 100 * \frac{O_2 (in) - y}{x - (O_2 (in) - y)}$$ (Equation. 1)

$O_2(calc)$ = oxygen concentration product;

$O_2(in)$ = oxygen concentration input.

For the maximum concentrations in the observation period parameters y = 11.7 and x = 0.629 were estimated. For the minimum concentrations the corresponding values were y = 12.6 and x = 0.709.

The addition of argon to ambient air leads to a more pronounced decrease (Figure. 3) of the oxygen concentration in the product than the former group of gases. Argon is concentrated

along with oxygen in the product gas. Therefore the concentration ratio argon/ oxygen remains almost the same.

The relationship described in Equation 1 can be corrected for the argon fraction in the input gas in order to predict the oxygen concentration from the oxygen concentration in the input gas:

$$O_2\,(calc,Ar) = O_2\,(calc)* \frac{O_2\,(in)}{O_2\,(in) + Ar(in)} * sep(O_2/Ar) \qquad \text{(Equation. 2)}$$

$O_2(calc,Ar)$ = oxygen concentration product in the presence of argon;

$O_2(calc)$ = oxygen concentration product according to Equation 1;

$O_2(in)$ = oxygen concentration input;

$sep(O_2/Ar)$ = 1.04, reflects the subtle differences in accumulation by the concentrator between oxygen and argon [6].

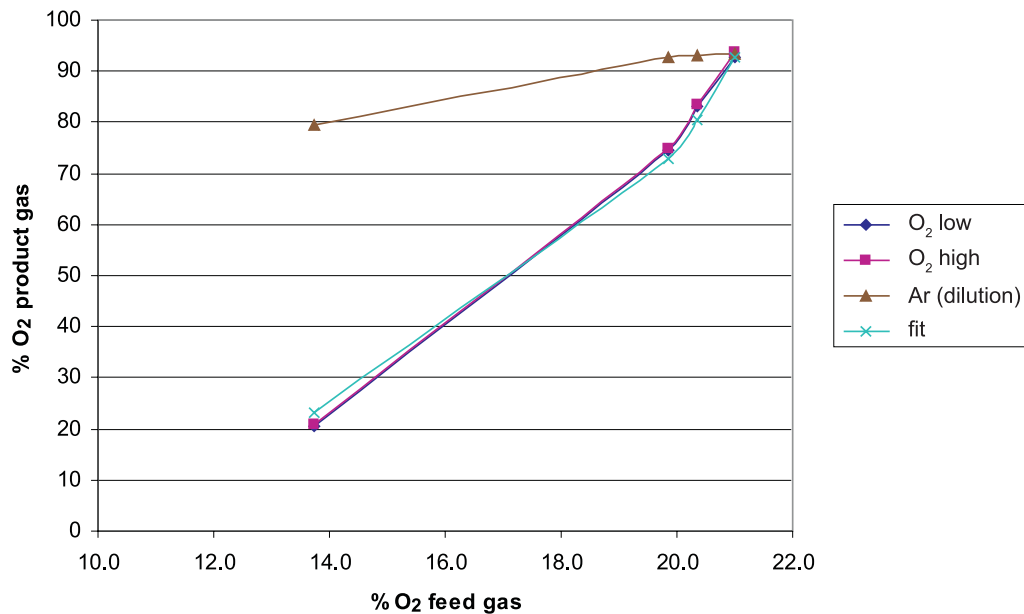Figure 3 – *Dilution effect of argon on the O_2 output concentration.*
O_2 low, O_2 high: observed oxygen concentrations.
'Dilution' refers to the expected O_2 concentration according to Equation. 1.
'Fit' refers to the expected O_2 concentration under the extended
argon effect according to Equation. 2.

For N_2, O_2, CO_2, CO and Ar the oxygen concentrations in the product after application of the contaminant always returned to the concentrations observed prior to the experiment. These gases apparently had no lasting effect.

In the case of NO_2 only 1 observation level at 9.8 % in synthetic air was realised. The O_2 concentration in the product decreased with time from 93.5 % to 92.4 % (O_2 high) and 92.4 % to 90.4 % (O_2 low) respectively. After cessation of the NO_2 input the oxygen concentrations in the product did not return to the previous levels during the observation period (Figure. 4).
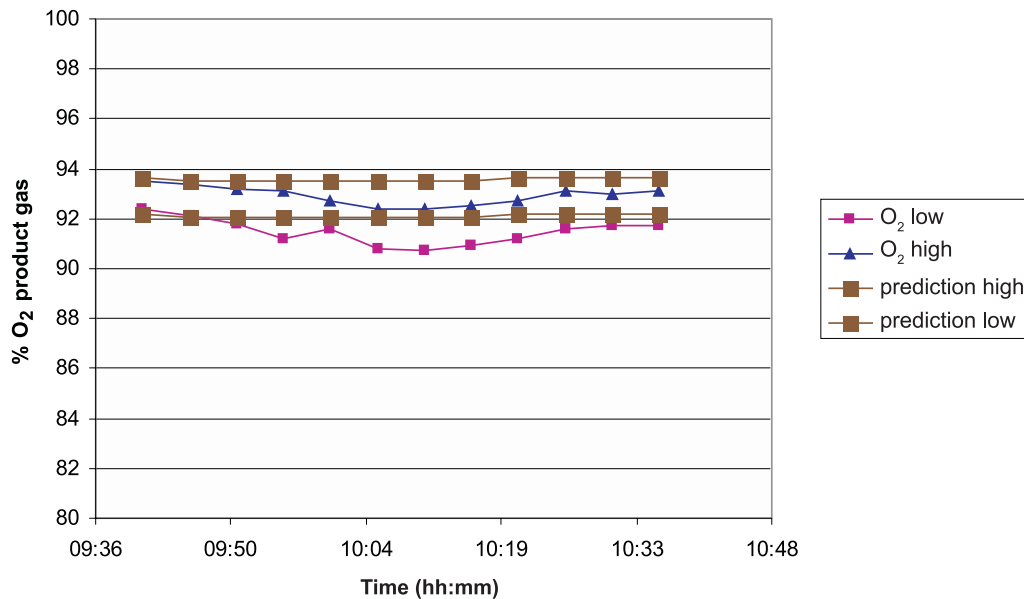
Figure 4 –   *Alteration of product gas composition under NO$_2$ input at 12.5 L/min.*
Start of NO$_2$ addition 9:41 h, end of NO$_2$ addition 10:21 h.
O$_2$ low, O$_2$ high: observed oxygen concentrations.
Prediction high, low: calculated oxygen concentrations according to Equation. 1.

The addition of NO to the feed gas leads to a vivid reaction with oxygen to give NO$_2$. Therefore the effective oxygen concentration in the input is considerably lower than the nominal concentration value calculated from the mixture ratio. Thus an increase of the NO concentration in the feed gas from 3 % to 6 % caused a decrease in the oxygen concentration from 87.1/84.1 % (high/low) to 72.4/69.6 % (high/low) even though the oxygen concentration in the input was kept constant at 19.9 % (Figure. 5).

The treatment of the oxygen concentrator with NO led again to a remaining decrease in the oxygen concentration in the product even after attempted regeneration with higher oxygen input.
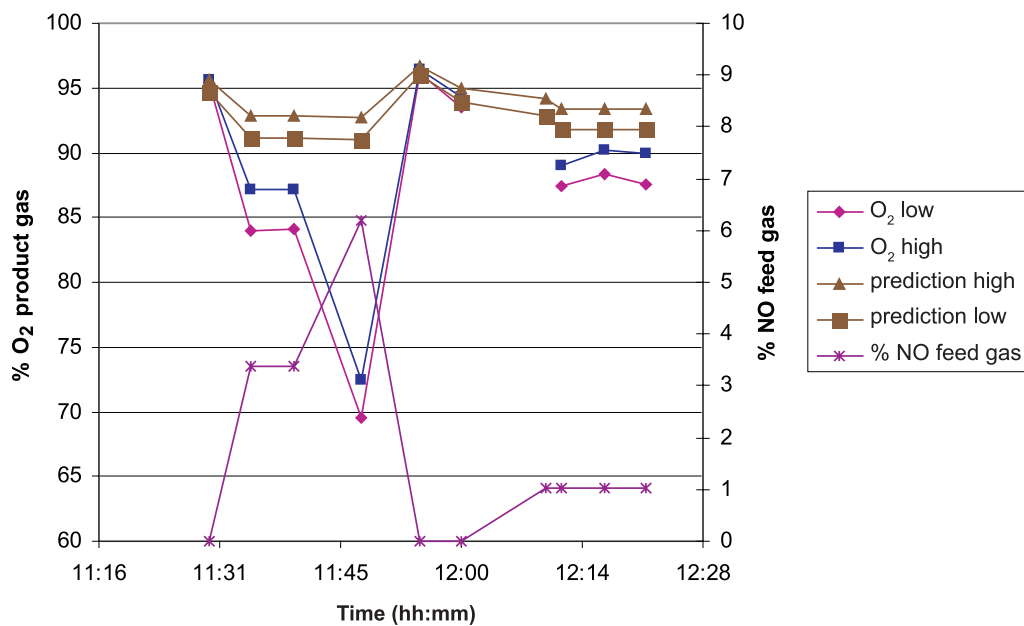

Figure 5 –   *Alteration of product gas composition under NO input.*
Start of NO addition 11:35 h, end of NO addition 12:22 h.
O$_2$ low, O$_2$ high: observed oxygen concentrations.
Prediction high, low: calculated oxygen concentrations according to Equation. 1.
% NO: corresponding NO concentration in the feed gas.

Following the treatment with NO the concentrator was exposed to increasing concentrations of SO_2. Again the decrease of the oxygen concentration in the product is more pronounced than expected from the predictions. Moreover a further persistent decrease in the performance of the module was observed after completion of the SO_2 exposition (Figure. 6).
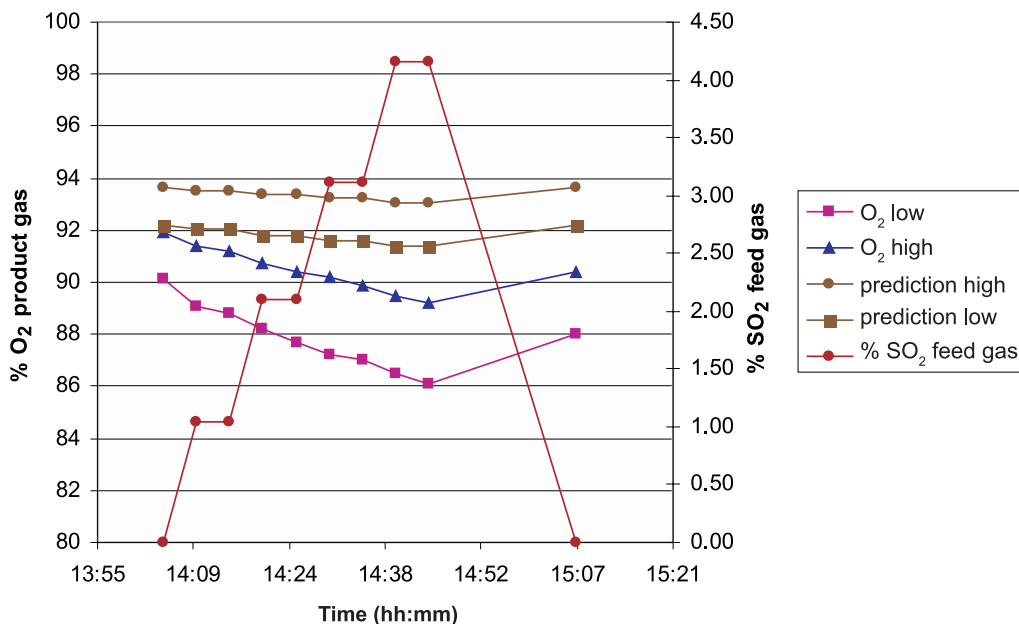

Figure 6 – *Alteration of product gas composition under SO_2 input.*
Start of SO_2 addition 14:10 h, end of SO_2 addition 14:50 h.
O_2 low, O_2 high: observed oxygen concentrations.
Prediction high, low: calculated oxygen concentrations according to Equation. 1.
% SO_2: corresponding SO_2 concentration in the feed gas.

3.2 Detection of contaminants in the product gas

Under the experimental conditions used in this work only CO was detected in the product gas.

CO appeared time delayed dependent on the CO concentration in the input. A maximum concentration of 152 ppm was measured (Figure. 7). Apparently a steady state was not yet reached when the CO administration was terminated.
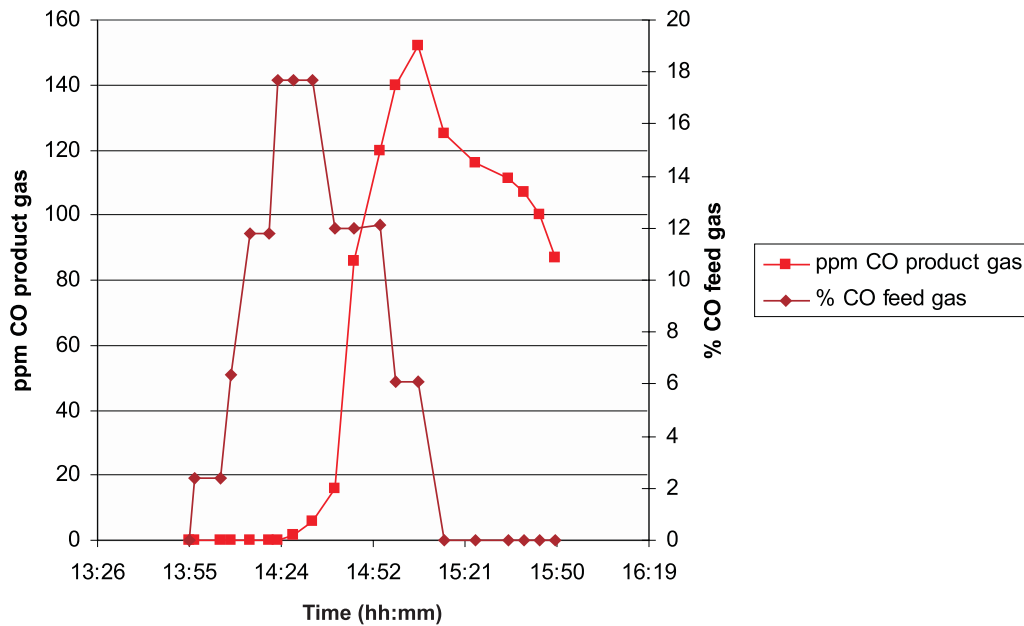
Figure 7 –   *Time course of CO in feed gas and product.*
             Start of CO addition 13:57 h, end of CO addition 15:15 h.
             ppm CO product gas: observed CO concentration.
             % CO feed gas: corresponding CO concentration in the feed gas.

In Table 2 the gas expositions are shown as flow rates and total challenges.

Table 2 – *Flow rates and total challenges of contaminants*

Gas	Max. flow (L/min) conc. Gas supply	Max. conc. feed gas (%)	Flow g/min	Cumulative challenge (mol)	Duration of challenge (min)	Occupational exposure limiting value (ppm)*
CO_2	21 (100 %)	16.5	40	23	10	5000
CO	75 (30 %)	17.7	26	44	18	30
NO_2	12.5 (10 %)	0.98	3	2	30	5
NO	60 (13 %)	6.2	11	6	7	25
SO_2	52 (10 %)	4.2	15	6	10	1

* TRGS 900 [7]

4. DISCUSSION

The experiments of this work were carried out with an oxygen concentrator module filled with zeolite A. The module was exposed to gas mixtures of widely varying composition and the impact of the various contaminants on the product gas was monitored. The concentrator is designed and optimised with regard to capacity, working pressures and pressure swing cycles to fulfil the requirements defined in the monograph 2455, Oxygen 93 per cent [1]. With

approximately 125 L/min ambient air (20.9 % O_2, 78.1 % N_2, 0.93 % Ar [2] and additionally on average 4 % (*V/V*) water) as feed gas this concentrator module generates approximately 10 L/min product gas containing 90-96 % O_2. Additional criteria are given in the monograph for CO_2 (< 300ppm), CO (< 5ppm), NO_x (< 2ppm) and SO_2 (< 1ppm).

During the experiments described in this work the concentrator was exposed to extreme conditions in terms of contaminant flow rates and total challenges (Table. 2). With CO_2, a rate of 40 g per minute was used which was completely separated into the waste gas. This corresponds to 20 g CO_2 per cycle which could be deposited on the adsorbent. In contrast the smaller amount of 13 g CO per cycle could not be completely retained (Figure. 7).

Challenges of 1.5 g NO_2, 5.5 g NO or 7.5 g SO_2 per cycle were also completely removed from the feed gas.

The fluctuations in the oxygen concentration of the product gas were unexpected in that other previously used modules had not shown such behaviour. The most probable explanation for this is a malfunctioning of at least 1 of the 12 columns. As a consequence maximum and minimum concentrations in the observation period had to be evaluated with regard to the requirements set in the monograph.

With a constant product gas flow, as in our experiments the main determinant for the O_2 concentration in the product gas is the O_2 concentration in the feed gas, e.g. less O_2 in, less O_2 out. The exact chemical composition of the feed gas is not relevant for this dilution effect.

The additional effect seen with Ar can readily be explained as a dilution of the product gas since argon is not retained but is enriched together with oxygen in the concentrator [6,8]. NO, NO_2 and SO_2 on the other hand probably react chemically with the zeolite packing in the presence of water [9,10]. This assumptive formation of mineral acids apparently reduces the overall performance of the concentrator, which could not be recovered by prolonged regeneration with air under normal conditions [10]. Moreover the consumption of oxygen by reaction with NO to give NO_2 [11] is not sufficient to explain the decrease in the oxygen concentration of the product gas.

If the oxygen concentration in the feed gas falls below a level of 18 % the corresponding oxygen concentration in the product under-runs the critical 90 % threshold. N_2, CO_2 and CO could be shown to solely exhibit this dilution effect. The NO_2 concentrations available were not sufficient to generate the required oxygen level in the input.

With the exception of CO, the monitoring of the 90 % threshold for O_2 in the product gas is sufficient to ensure concentration levels of the contaminants investigated are below the critical concentration levels defined in the monograph. In the case of CO concentrations in the feed gas above 12 % corresponding to 18.5 % oxygen, this will cause CO concentrations in the product to greatly exceed the 5ppm threshold (Figure. 7). With these CO levels the oxygen concentration in the product will still be above 90 %. While in practice a concentration of 12 % CO would never be reached in ambient air as a worst case scenario it is conceivable that fire effluents can lead to such CO concentrations in the input. Therefore in-process CO monitoring in the feed gas is considered a possible remedy. Further experiments would be required to determine a no effect level for CO. From Figure. 7 it can at least be deduced that at a CO input level of 12 % the corresponding concentration in the product gas will be well below 150 ppm.

The additional effects of NO, NO_2 and SO_2 are based on chemical reactions. While in this work no direct evidence for such reactions was obtained a wealth of information is available in the literature [9, 10, 11, 12, 13, 14]. Physico-chemical processes on the adsorbents are determined by pre-treatment of the zeolite, temperature, flow and composition of the gas mixture [3]. Some authors discuss the formation of nitrates on the adsorbing surface which provides a possible

explanation for the observed lasting decrease in the concentrator performance since nitrates cannot be evaporated by PSA [10].

An analogous mechanism can be proposed for SO_2 with the formation of sulphites or sulphates [15].

The production of oxygen 93 % by PSA is a continuous process which cannot be monitored by the offline analysis of production batches. The present test procedures rely on the availability of ambient air of sufficient quality. To assure compliance with the O_2 93 % monograph even under extreme conditions, i.e. for unusually high concentrations of contaminants a two-fold approach is suggested:

1. Monitoring of the 90 % threshold for O_2 in the product gas. This takes care of dilution effects of contaminants as well as additional effects due to chemical reactions.
2. Monitoring of the CO concentration in the input gas with a suitable warning level, for which compliance with the monograph has been established. According to our findings this could be in the range of 1-3 % CO in the feed gas and therefore be subject to further experimental verification.

No conclusive information was available from our experiments with regard to the long-term behaviour of the concentrator module when exposed to moderate or high concentrations of contaminants. In any case if a continuous decrease over time of the performance of the concentrator occurs the 90 % critical value will be eventually underrun.

5. CONCLUSION

Oxygen concentration in the product gas was primarily a function of the oxygen in the feed gas. Ar, CO, CO_2 and N_2 in the feed gas reduced the oxygen concentration and led thus to a corresponding reduction of the oxygen concentration in the product gas. Additional effects due to chemical reactions were observed with NO_x and SO_2. These effects led to a further reduction of the oxygen concentration in the product gas.

The main objective of this work was to assess whether measurement of oxygen alone is sufficient to establish the required purity and content. Under the experimental conditions of this work only CO was detected in the product gas in addition to oxygen, N_2 and Ar. It can presently not be excluded that the 5 ppm level for CO in the product gas will be exceeded before the dilution effect of CO will lead to a decrease of the oxygen concentration below 90 %. For this situation appropriate CO monitoring of the input gas is considered a possible remedy.

Exposure to NO_x and SO_2 under the experimental conditions of this work caused an irreversible decrease in the performance of the module.

6. ACKNOWLEDGEMENTS

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