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Acid Gas Removal by Customized Sorbents for Integrated Gasification Fuel Cell Systems

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Introduction

Power generation from coal by Integrated Gasification Combined Cycle (IGCC) is the focus of research efforts in many countries. Large-scale coal gasification processes are commercially available. Current research and development is focusing on biomass gasification for energy production in the small and medium sized range (Kurkela 1996). The generation of energy from fossil fuels and the associated greenhouse gas emissions have created environmental and energy policy pressures to increase the efficiency of fossil fuel based systems and to enhance the utilization of renewable energy generation. Despite the remarkable progress, which has been achieved in recent years, gas cleaning is still the bottleneck in advanced gas utilization that limits the development of Integrated Gasification Fuel Cell Systems (IGFC) based on coal or biomass (Kaltschmitt et al. 1998). Thus, it is of great importance to advance hot gas cleaning to make IGFC with high temperature fuel cells a more feasible and attractive energy generation alternative (Heinzel et al. 1999).

Different fuel cell types are under development. They all operate by feeding a hydrogen rich stream to the anode and a oxygen rich stream to the cathode of the fuel cell. The hydrogen and oxygen then react electrochemically, producing water and electricity. The possible fuels vary depending on the fuel cell type, and each fuel cell has a specific range of operating temperatures (Mahlendorf et al. 1999).

Molten Carbonate Fuel Cells (MCFC) and Solid Oxide Fuel Cells (SOFC) operate at high temperatures and can tolerate higher amounts of impurities in the product gas than do low temperature fuel cells. Thus, MCFC and SOFC are more appropriate for IGFC systems be-

cause of more suitable fuel gas composition requirements and lower exergy losses (Knight et al. 1998). Variation in coal and biomass compositions represents a fundamental problem with regard to the gas cleaning system. Gas produced from these feedstock contains sulfur and hydrogen halides, which may cause degeneration of the steam reforming and the fuel cell catalysts. Thus, acid gas removal systems have to attain high removal efficiencies for these impurities to ensure proper operation of the fuel cell (Hutter, Krammer 2000).

Objective

In order to reduce exergy losses, gas cleaning at high temperatures is favored in IGFC systems. As shown by thermodynamic data, separation efficiencies of common sorbents decrease with increasing temperature. Therefore, acid gas removal systems have to be developed for IGFC applications considering sorbent capacity, operation temperature, gasification feedstock composition and fuel cell threshold values.

Approach

Possible temperature ranges of acid gas removal systems in IGFC systems are restricted by thermodynamics. Therefore, thermodynamic calculations were carried out to evaluate the performance of different sorbents used in high temperature gas cleaning applications for IGFC systems based on biomass or coal. Due to the limitation of exergy losses, the study focused on the temperature dependence of the obtained gas quality of fuel gas before entering the fuel cell stack. The derived operating temperatures can serve as a basis for the design of a hot gas clean up.

Thermodynamic calculations using EquiTherm™ software were carried out for a typical fuel gas of autothermal, fluidized bed wood gasification systems. The gas contains 12 % CO, 14 % CO₂, 12 % H₂, 15 % H₂O, 47 % N₂, 200 ppm HCl, 200 ppm H₂S and 10 ppm HF at ambient pressure.

Calcium based sorbents with calcium carbonate as active component can be used for simultaneous removal of sulfur components and hydrogen halides. Nevertheless, calcium carbonate is not an appropriate sorbent if product gases of biomass gasification with high CO₂ and H₂O contents are used. Therefore, calcium carbonate was not considered in this project.

Removal of hydrogen chloride (HCl) and hydrogen fluoride (HF) was investigated for sodium carbonate (Na₂CO₃) and sodium aluminate (NaAlO₂) sorbents whereas tin oxide (SnO), iron oxide (Fe₂O₃) and zinc oxide (ZnO) were investigated for hydrogen sulfide (H₂S) removal.

Project Description

With respect to the given raw gas composition and the fuel cell requirements, the maximum operating temperature of the hydrogen halide removal system is limited by the HF removal efficiency. Figures 1 and 2 illustrate the HF and HCl equilibrium concentration as a function of temperature for given sorbents.

Sodium carbonate shows the lowest temperature dependence so that the outlet hydrogen halide concentrations do not decrease with decreasing temperature to the same extent as for sodium aluminate. MCFC fuel cells require fuel gas purities of up to 0.01 ppm HF and 0.1 ppm HCl, whereas SOFC fuel cells can tolerate 1 ppm hydrogen halides. As a result, the maximum operating temperatures of sodium carbonate based hydrogen halide removal systems are about 300 °C for SOFC and less than 200 °C for MCFC systems. In the latter temperature

range, wet hydrogen halide removal systems might be more appropriate. Maximum permissible temperatures of sodium aluminate are about 300 °C for MCFC and 450 °C for SOFC fuel cell systems. Considering thermal integration of the gas cleaning process into IGFC systems, sodium aluminate is preferred for dry hydrogen halide removal in these systems.

Respective calculations were carried out to obtain desulfurization efficiencies for SnO, Fe₂O₃ and ZnO. The results show that the Water Gas Shift Reaction (WGSR) has a major influence on desulfurization. WGSR (reaction 1) is exothermic and, therefore, thermodynamically unfavorable at elevated temperatures. If the temperature range of gas cleaning is lowered, WGSR might have a positive effect on separation efficiencies for H₂S removal by metal oxides (reaction 2 to 4). In contrast to desulfurization, hydrogen halide removal showed only a very weak correlation between equilibrium HCl and HF concentration and WGSR.



If WGSR occurs and what the equilibrium concentrations are depends not only on the temperature, but also on many other factors like competing reactions etc. Thus, in the investigations two marginal cases were considered: complete WGSR and no WGSR at all. The influence of WGSR is evident by comparison of figures 3 and 4, which show the H₂S equilibrium concentration as a function of temperature and sorbents. WGSR is taken into consideration in figure 3 but not in 4.

Considering the given raw gas composition and WGSR, SnO clearly showed the poorest performance and did not meet the H₂S purification requirements of 1 ppm for SOFC and 0,1 ppm for MCFC systems even for temperatures lower than 200 °C. Therefore, SnO does not seem to be appropriate for desulfurization in IGFC systems. Compared to SnO, Fe₂O₃ showed lower H₂S equilibrium concentrations with regard to desulfurization, even though required fuel gas purity could only be attained for temperatures below 300 °C for SOFC and below 200 °C for MCFC. Remarkably higher desulfurization temperatures of 450 °C for SOFC and 300 °C for MCFC were obtained with ZnO used as sorbent. From these results, it seems quite conceivable that for the given raw gas composition, HCl, HF and H₂S removals might operate in the same temperature range.

Similar to WGSR, the moisture content of a given raw gas has an influence on acid gas removal. Figure 5 shows the H₂S equilibrium concentration as a function of temperature and water content if ZnO is used as sorbent for H₂S removal. In the range of 10 to 20 % H₂O content of the fuel gas, the possible temperature range of gas cleaning, which is determined by threshold values of MCFC and SOFC and H₂S equilibrium concentrations, differs by about 50 °C.

Results

Results of thermodynamic calculations confirm that hot gas cleaning systems based on dry acid gas removal are appropriate to meet the requirement of MCFC and SOFC in IGFC systems using biomass or coal as feedstock. Nevertheless, significant gas cooling is necessary.

Operating temperatures are restricted by HF equilibrium concentrations and threshold values of the fuel cells. Therefore, the threshold values of MCFC and SOFC play a major role for determination of operating temperatures for halide removal.

Due to substantial fuel cell costs and limited experience, currently lower threshold values for impurities in fuel gases are defined than actually might be necessary. Threshold values for acid gases, especially for hydrogen halides, might be raised if fuel cell technology advances, which can influence process design and, in particular, operating temperatures of acid gas cleaning systems.

Application

Hot gas cleaning for IGFC systems with sorbents might offer cost and efficiency benefits compared to conventional wet cleaning technologies. Techniques for the removal of hydrogen sulfide have been developed and demonstrated on commercial scale plants. However, systems for hydrogen halide removal still require substantial development.

Future Activities

Considerable progress has been made in different areas of IGFC process development in recent years. However, up to now, a technically and economically optimized system including gasification, gas cleaning and gas utilization in fuel cells has not been demonstrated.

Therefore, a multistep purification process to reduce tars, alkali metals and dust as well as acid gases, which is appropriate for different kinds of IGFC systems has to be developed. It is proposed to combine the multistep purification process with biomass gasification. These activities should be focused on Integrated Biomass Gasification Fuel Cell systems for small to medium scale applications.

References

- Heinzel, A., et al., 1999. Biomasse-Vergasung für Brennstoffzellen. Österreichische Elektrizitätswirtschaft-Aktiengesellschaft. Schriftenreihe der Forschung im Verbund Band 59.
- Hutter, C., Krammer, T., 2000. Stationäre Anwendung von Brennstoffzellen in der Kraft-Wärme-Kopplung (Teil 2). Koordinationsstelle der Wasserstoff-Initiative Bayern.
- Kaltschmidt, M., et al., 1998. Biomass Gasification in Europe. Institute of Energy Economics and the Rational Use of Energy.
- Knight, R., et al., 1998. Fuel Cell Power Plants Using Hydrogen from Biomass. *Proceedings of the American Power Conference* 60 (1): 586-591.
- Kurkela, E., 1996. Formation and Removal of Biomass-Derived Contaminants in Fluidized-Bed Gasification Processes. Technical Research Centre of Finland.
- Mahlendorf, F., et al., 1999. Brennstoffzellen – ein Überblick. 6. Fachform Einsatz von Brennstoffzellen. Ostbayerisches Technologie-Transfer-Institut e.V. (OTTI).

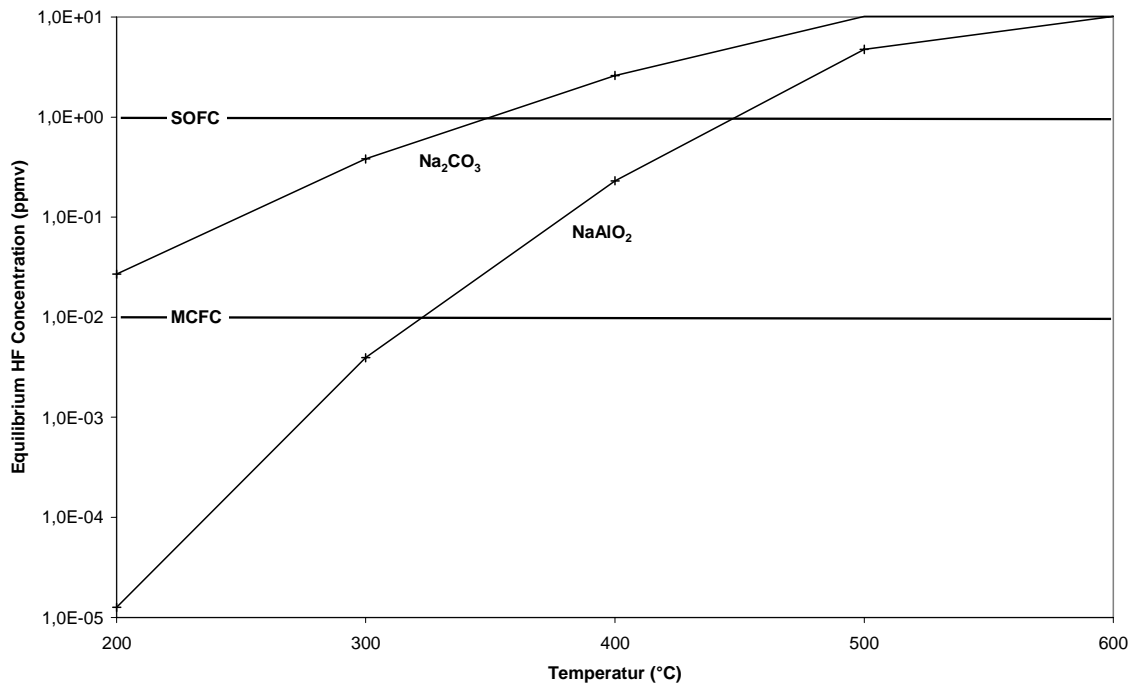


Figure 1: Equilibrium HF concentration. Water gas shift reaction allowed. (Gas composition: 12% CO, 14% CO₂, 12% H₂, 15% H₂O, 47% N₂, 200 ppm HCl, 10 ppm HF)

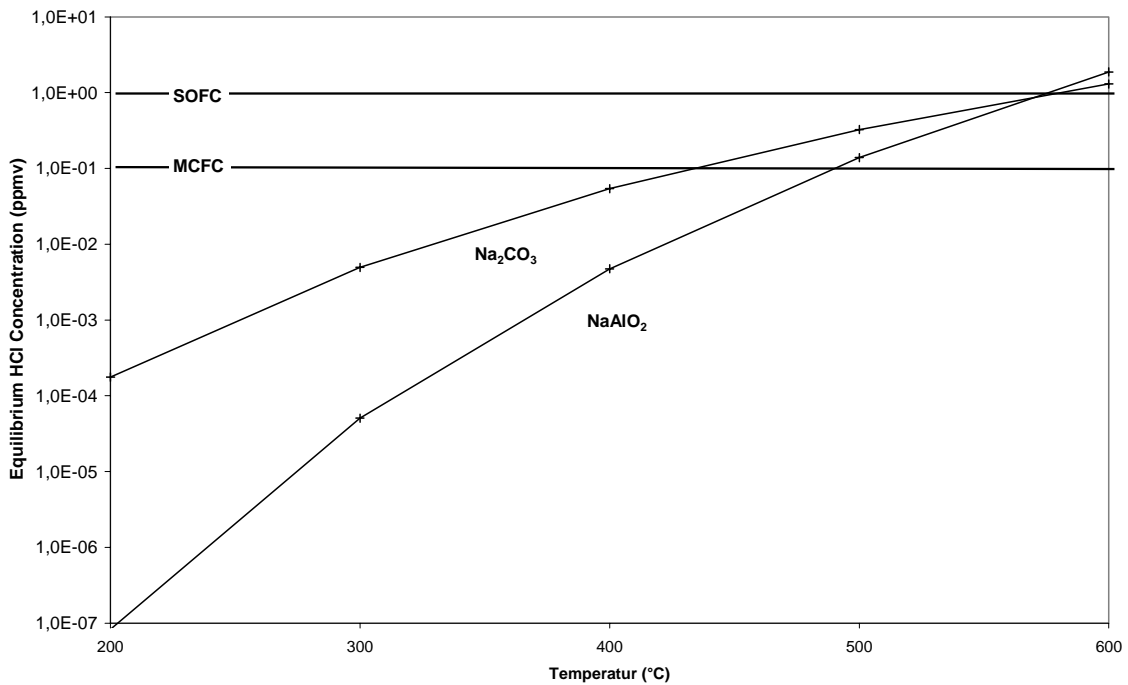


Figure 2: Equilibrium HCl concentration. Water gas shift reaction allowed. (Gas composition: 12% CO, 14% CO₂, 12% H₂, 15% H₂O, 47% N₂, 200 ppm HCl, 10 ppm HF)

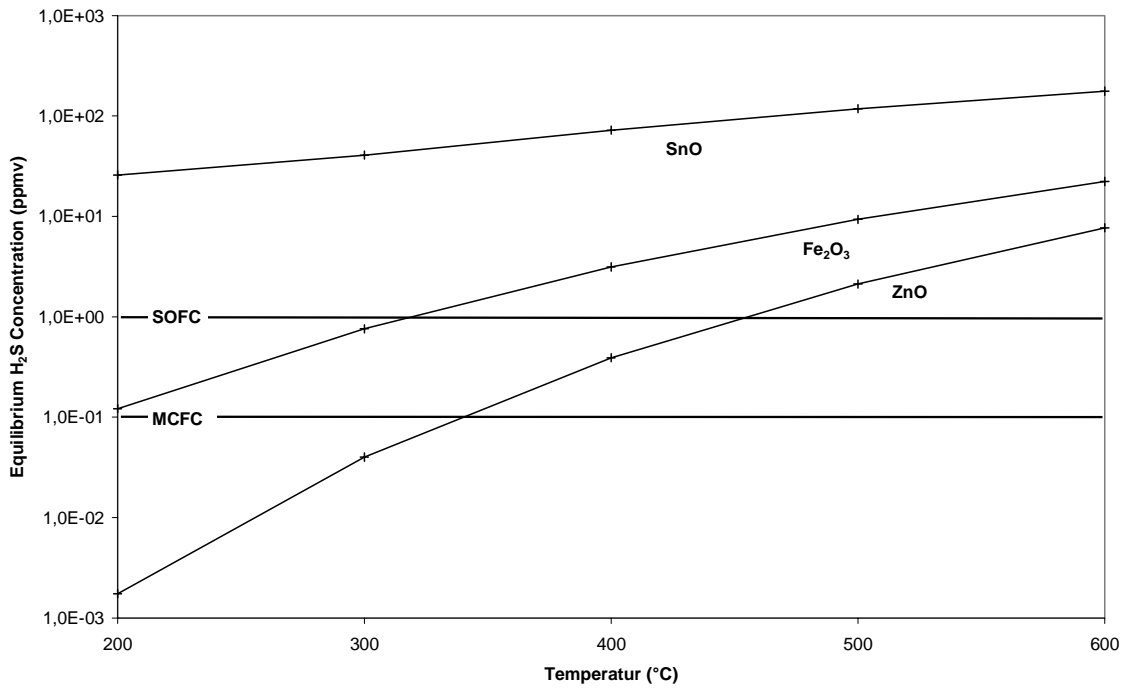


Figure 3: Equilibrium H₂S concentration. Water gas shift reaction allowed. (Gas composition: 12% CO, 14% CO₂, 200 ppm H₂S, 15% H₂O, 47% N₂)

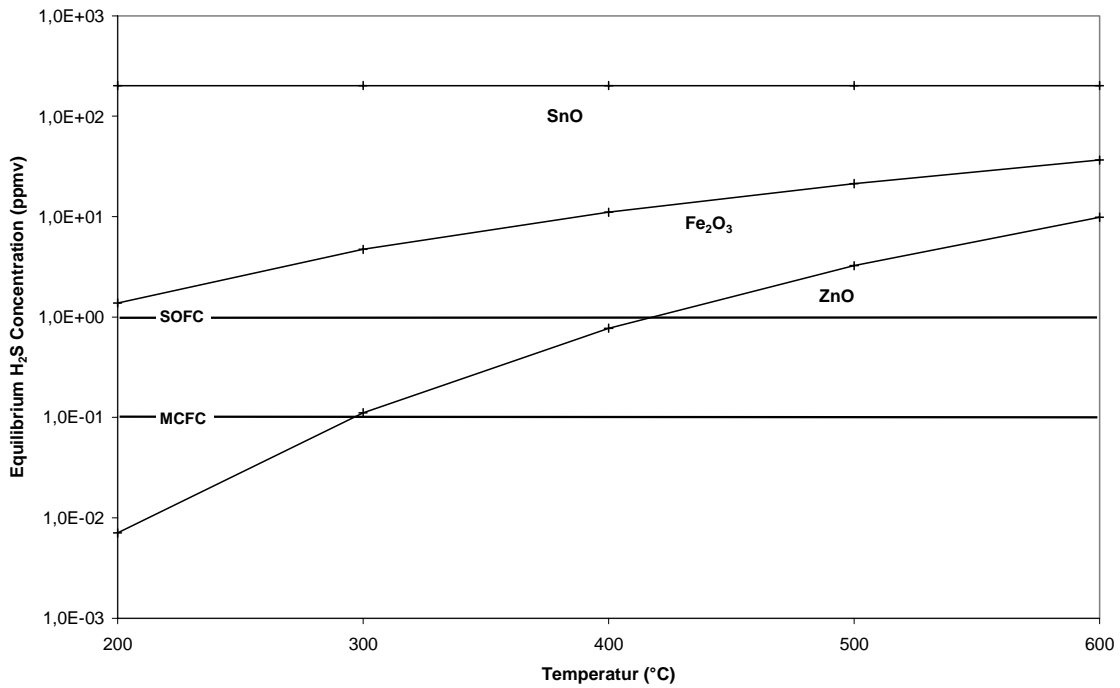


Figure 4: Equilibrium H₂S concentration. Water gas shift reaction not allowed. (Gas composition: 12% CO, 14% CO₂, 200 ppm H₂S, 15% H₂O, 47% N₂)

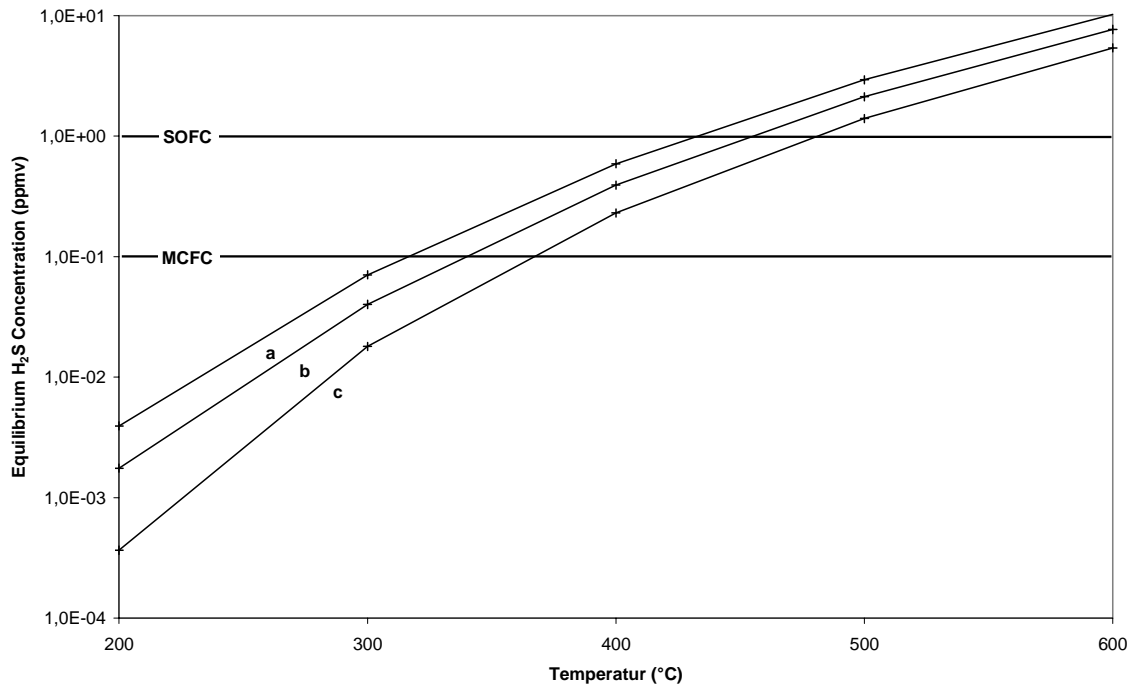


Figure 5: Equilibrium H₂S concentration for desulfurization by ZnO (Gas composition: 12% CO, 14% CO₂, 12 % H₂, 200 ppm H₂S, (a) 20% H₂O, (b) 15% H₂O, (c) 10% H₂O, bal. N₂)