6.1 Summary and conclusions

Source gases that are used in subsurface CO₂ sequestration such as flue gas of power plants and acid gas as a waste product of oil production, do not consist of pure CO₂, but contain additional gases. Removal of these ‘impurities’ is a rather costly element in the chain of steps that are required to store CO₂ in the subsurface. Apart from these impurities, the CO₂ that is injected in subsurface also encounters ambient (non-CO₂) gases that exist in the storage reservoir.

In this thesis research is presented that addresses the impacts of impure gas compositions for the storage of CO₂ in depleted hydrocarbon reservoirs and saline aquifers. In general these impacts can be divided into two main categories: physical and chemical. Physical effects concern conditions and processes such as phase behaviour, storage capacity, wellbore injectivity, permeation flux, buoyancy, etc. Chemical effects include rock-water (geochemical) reactions, caprock integrity, corrosion of well materials, hazardousness in the event of leakage, etc. Although the work presented in this thesis is far from exhaustive on all of these potential impacts, results include both novel tools to address such impacts and new insights into a number of physical and chemical effects of impurities.

Chapter 1 introduces the principle of Carbon Capture, transport and Storage (CCS) as one of the methods to reduce the CO₂ of industrial sources to the atmosphere that are invoked to mitigate climate warming associated with the ‘greenhouse effect’ of this gas. Additionally, the present use of CCS for storage in depleted hydrocarbon reservoirs and saline aquifers around the globe and in the Netherlands is elucidated in this chapter, and the aims and foci of the present research are specified.

The conclusions of each chapter are summarized as follows:

- In chapter 2 a new non-iterative and accurate EOS has been presented (fully documented) for gas mixtures in equilibrium with brine. The EOS allows calculation of the composition of the gas mixtures in both the aqueous and the non-aqueous phase for a large range of pressure (1-600 bar), temperature (1-110 ºC) and salinity conditions (up to 6 M). The gas mixtures can include CO₂, SO₂, H₂S, CH₄, O₂ and N₂ (gases that occur in flue gases, in acid gas, or in-situ in a gas reservoir). In the model, the Peng–Robinson EOS is used to calculate the fugacity of the gas phase, but it can be easily modified to include another cubic EOS such as SRK. The model has been shown to perform favorably with respect to existing EOS’s and experimental data for single gas systems, and it accurately reproduces available data sets for gas mixtures. Predictions with this model show that the amount of dissolved CO₂ is most sensitive (negatively) to CH₄. Presence of SO₂, by contrast, can enhance the amount of dissolved CO₂.

- In chapter 3, first methods were developed to calculate transport properties such as density, heat capacity and viscosity of both aqueous and non-aqueous phases for single gases and gas mixtures. Then, as one of the physical effects of impurities, the Joule-Thomson Cooling (JTC) effect in depleted hydrocarbon reservoirs was studied by using coupled heat and mass transport modeling with accurate pressure-, temperature-, and gas-compositional dependency of the thermo-physical transport properties. Injection of pure CO₂ causes JTC-cooling (due to expansion of the gas) as it spreads into the reservoir. It was found that presence of gases other
than CO₂ (impurities) affect both the spatial extent of the zone around the well bore in which this cooling occurs and the magnitude of cooling. These two effects are predominantly controlled by the specific heat capacity and the density of the gas mixture, respectively. SO₂ can expand the zone of cooling, O₂, N₂, and CH₄ can contract this zone, and H₂S has a very small influence on the spatial extent of cooling. However, the operational conditions of gas injection can play an important role in these behaviours. Enhanced cooling (up to 5 °C) is caused by O₂, N₂, and CH₄ in combination with constant pressure injection, while for constant rate injection cooling enhancement is minimal or absent. However, the thermal risks associated with co-injection of these impurities for hydrate formation (this might clog pores and potentially impair injectivity) appear small. Co-injection of SO₂ has beneficial thermal consequences by suppressing JTC.

- **In chapter 4**, the sensitivity of the CO₂ storage capacity (STC) to the presence of impurities (H₂S, CH₄, O₂, N₂, Ar and SO₂) was investigated for both solubility trapping (in the aqueous phase) (STCS) and volumetric trapping (in the non-aqueous phase) (STCV). It was found that binary mixtures of CO₂-SO₂ exhibit anomalous storage effects when compared to other common impurities; while other gases reduce CO₂ storage in the aqueous and non-aqueous phase, SO₂ can increase both forms of CO₂ storage. SO₂ enhances CO₂ volumetric trapping significantly for relatively low temperatures that are representative for shallow (< 1 km) aquifers, and in deeper depleted hydrocarbon reservoirs during the injection stage. Solubility trapping, by contrast, is mostly enhanced by SO₂ for relatively high pressures (deep aquifers), while at pressures larger than 100 bar it is relatively insensitive to temperature. Presence of SO₂ is further expected to enhance the gas dissolution rates (transfer from non-aqueous to the aqueous phase) due to its marked influence on brine density and free convection. For multi-component impurity mixtures such as oxyfuel flue gas, addition of SO₂ can compensate for the negative impact of the other impurities. These findings suggest that the positive effects of SO₂ on the CO₂ storage capacity could be of practical significance for CCS projects.

- **In chapter 5**, the new EOS (Chapter 2) was used in conjunction with the geochemical modelling code PHREEQC to study the long-term geochemical impacts of impure CO₂ storage in a saline aquifer. The 1D model simulates the dissolution of the component gases of an impure CO₂ store at a gas-brine interface, and subsequent diffusive transport of the gases into the brine together with the associated aqueous and water-rock interactions. This system provides an approximate representation of post-injection conditions where flows of the non-aqueous phase and the brine have become small and diffusive transport predominates. The mineralogy of the Triassic Hardegsen Formation at the P-18 gas-field in the Dutch offshore was used for the mineralogy of the aquifer storage simulations (it is important to emphasize that these simulations are not representative for CO₂ storage in depleted gas fields like P-18). After 10,000 yr, irrespective of the gas composition, very large porosity reduction is predicted up to about 10 m from the gas-brine interface and a slight porosity increase at larger distances. For pure CO₂, the original reservoir porosity (0.11) is reduced to virtually zero (0.0002) at the interface by precipitation of quartz and large amounts of dawsonite. Presence of O₂, N₂, Ar or
combinations thereof, such as in oxyfuel flue gas, and presence of CH₄ have very little effect on the geochemical response. Presence of SO₂ induces complex changes, including a strong reduction or absence of dawsonite precipitation near the interface, precipitation of kaolinite and anhydrite near the interface, and anhydrite and dawsonite precipitation some distance (~5m) from the interface. Porosity is enhanced near (to 0.03 for 4% SO₂), but strongly reduced away from the interface mainly due to anhydrite precipitation. The geochemical effect of H₂S shows similarities with that of SO₂, but with smaller magnitude and impacts only become significant for large mass fractions > 3%. However, the predicted behaviors are expected to be rather sensitive to the primary mineral assemblage and their individual contents and, therefore, do not have broad applicability to aquifers with other geochemical compositions.

6.2. Recommendations

A recurring feature in the chapters of this thesis is the paucity of experimental data for gas mixtures and for some of the impurity gases. In Chapter 2 for instance, the lack of solubility data of SO₂ in water and brine and for the water-content of the SO₂-rich phase for relevant pressures and temperatures was highlighted. Similarly, limited data for H₂S at pressures in excess of 200 bar and the overall paucity of experimental data on solubility and water content of gas mixtures was documented. This implies that EOS’s that are essential for impurity-impact assessments, such as the one developed in this work, remain relatively poorly constrained for important ranges of PT-conditions. Additionally, more experimental data for transport properties (density, heat capacity, viscosity) of both aqueous and non-aqueous phase gas mixtures are needed (Chapter 3) to improve the accuracy and reliability of predictions of reservoir behavior and of related parameters such as the CO₂ storage capacity of aquifers and depleted hydrocarbon reservoirs (Chapter 4). The fact that the methods/models developed in this thesis are fully documented allows for efficient updates of the models when relative new data become available in the coming years.

For CO₂ storage in very deep aquifers or hydrocarbon reservoirs with ambient temperatures in excess of 110 ºC the EOS developed in this thesis may not be sufficiently accurate. This is due to model parameterization rather than lack of data. It would, therefore, be worthwhile to adjust the EOS to also allow usage at these higher temperatures.

Since reliable EOS’s for the extensive set of gas mixtures and brine considered in this study were not available through conventional, advanced reservoir simulators, and coupling of the newly developed EOS to such simulators is a laborious task, analyses involving transport processes have remained relatively simple in the work presented in this thesis (Chapters 3 and 5) and many opportunities remain to expand modeling capabilities and impact assessment. An obvious advance would be to allow multi-dimensional (2D/3D) simulations. This would be particularly relevant for coupling with buoyancy-driven flows in aquifer storage and to assess the role of reservoir heterogeneity. Important therein is accurate compositional simulation; that is, multi-phase transport of multi-component mixtures. This requires a great deal of attention to ensure consistent partitioning of the multiple gas species and water among the aqueous and non-aqueous phases during transport. Preferential transfer of individual
component gases between aqueous and non-aqueous phase due to the different solubilities of the component gases should allow continuous adjustment of the gas composition of both phases which, in turn, feeds back to transport. The simulations of Joule-Thomson cooling presented in Chapter 3, for instance, were conducted for an invariant gas composition and absence of water. It would be of great value to know to what extent compositional simulation, including development of a dry-out zone around the well bore, would modify the predicted reservoir thermal response.

In recent years there has been considerable attention for the role of free convection as a factor which enhances the rate at which CO$_2$ stored in aquifers is dissolved in the brine. In Chapter 4 it was shown that the density of brine at the gas-brine interface in aquifers is very sensitive to the presence of some impurities, and in particular SO$_2$. This shows that impurities may have an important effect on the timescale at which the injected gas becomes trapped in the aquifer brine and subsequently in secondary minerals.

In closing, the work presented in this thesis has highlighted that impurities can have both positive and negative consequences for CO$_2$ storage. Most impurities (N$_2$, O$_2$, CH$_4$ and Ar) have a number of negative physical impacts. They tend to enhance Joule-Thomson cooling and reduce the CO$_2$ storage capacity. H$_2$S can have variable physical consequences depending on the impurity amount, and reservoir and operational conditions. Sulfur dioxide (SO$_2$), by contrast, was generally found to have positive consequences both for Joule-Thomson cooling and CO$_2$ storage. For the aquifer mineralogy adopted in the geochemical impact investigation in this thesis (Chapter 5), no clear negative impacts of presence of impurities were deduced. Overall, these results show that under favorable conditions, storage of impure CO$_2$ may be a viable option to reduce the overall costs of reservoir storage of CO$_2$ through savings in purification of source gases.