During ASR-cycle testing at a site in the confined Chalk near Lytchett Minster in Dorset, the high concentration of fluoride in the recovered water posed severe limitations on the success of the scheme. Based on physical modelling, the dual porosity character of the Chalk combined with high fluoride concentrations in the native water were identified as the key factors controlling the measured concentrations. However, mixing of water between the matrix pores and fractures was not sufficient to explain the fluoride concentration and it was concluded that there was an additional release of fluoride from aguifer interaction. This led to an additional increase in the fluoride concentration in the recovered water. In order to investigate this hypothesis, a geochemical model incorporating reactions between the injected water, the native groundwater and the aquifer minerals was developed. The geochemical model PHREEQC-2 was set up so that it was capable of modelling ASR-cycles (including radial flow and diffusive mixing as a consequence of dual porosity). The physical aspects of the model were calibrated using a 3-D dual porosity transport model (SWIFT). Different geochemical processes (e.g. limited mineral availability, reaction kinetics) causing fluoride concentrations above those expected from dual porosity mixing were investigated. Comparing the modelled results with the observations from the test site suggested that slow dissolution of fluoride minerals (fluorite) was likely to be responsible for the additional increase in fluoride concentration in the recovered water