The various phases of $CaSO_4 \cdot xH_2O$ ($0 \leq x \leq 2$) have different solid state transformation behaviour in the presence of varying Na^+/K^+ ratios. It was found that a naturally sourced brine and synthetically prepared brine resulted in very different final sulphate phases to form after the precipitation reaction, which were $K_2Ca_5(SO_4)_6 \cdot H_2O$ (görgeyite) and $CaSO_4 \cdot 0.6H_2O$ (non-stoichoimetric bassanite) respectively. To investigate the process of the different sulphates' formation, in-line Raman spectroscopy was used to monitor the precipitation reactions at various temperatures and multivariate curve resolution (MCR) was used to deconvolute the reaction profiles for the various solid and dissolved phases. The precipitated solids were also fully characterized off-line by TGA, Raman and FTIR spectroscopies as well as X-ray powder diffraction to ensure that the MCR results are interpreted correctly. The use of in-line Raman spectroscopy allowed for the monitoring of the different phases directly, compared to off-line sampling and analysis, removing uncertainty of what is happening in real-time.