Complex, hypersaline brines originating from the mining and extractive metallurgical industries have the potential to be treated using Eutectic Freeze Crystallization (EFC). Although EFC has been shown to be effective in separating a single salt and water, it has yet to be applied to the complex hypersaline brines that are typical of reverse osmosis retentates in South Africa. This paper focuses on the application of EFC for the purification of a typical brine containing high levels of sodium, chlorine, sulphate and ammonia that cannot be achieved with other separation techniques. The presence of ammonia prevents the application of membrane technology to treat the brine, leaving only cooling or evaporation as other possible options. Evaporation produces a mixed salt that requires further treatment. Modelling tools were applied to describe the phase behaviour of the complex saline systems under different process conditions and were experimentally validated. The results showed that Eutectic Freeze Crystallization could be used to selectively recover the sodium as a sodium sulphate salt. The simulation tools were especially useful in the design and optimisation of the process.