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The WRC operates in terms of the Water Research Act (Act 34 of 1971) and its mandate is to support water research and development as well as the building of a sustainable water research capacity in South Africa.

TECHNICAL BRIEF

Industrial water treatment

Treating multi-component hypersaline brines using eutectic freeze crystallisation

A completed WRC-funded project has successfully demonstrated the use of eutectic freeze crystallisation to treat multi-component brines.

Background

Hypersaline inorganic brines are generated by a number of industries, including mining operations, power generation and petrochemical refining. In addition, because of pressures on water resources, and thus further water recycling and reuse, these brines present an increasingly significant global problem.

Eutectic freeze crystallisation (EFC) has been identified as a possible novel brine treatment method, but to date it has not been applied to multi-component streams such as brines. Therefore, the overall aims of this WRC-funded project was to investigate the applicability of EFC to the multi-component hypersaline brines produced by major South African industries.

The first objective was to establish the thermodynamic and kinetic factors governing the operation of a sequential EFC process. The second objective was to summarise the effect of real brines compared to synthetic brines on the operation and control of an EFC process. For the third objective, the effect of impurities and contaminants on the ice product formed during an EFC process was investigated. The last objective was to investigate how operating temperatures affect the yield and purity of the final products formed in an EFC process.

Methodology

Four brines were studied overall: two from the coal-mining industry (Brine 1 and Brine 2) and two different brines from the platinum-mining industry. A comprehensive brine analysis had to be conducted before the thermodynamic modelling of the brine could proceed.

A combination of standard water analysis techniques and wet chemistry were used to characterise the brine, while a commercial thermodynamic modelling package (OLI Stream Analyser) was used to perform the thermodynamic modelling of the brine.

Results and discussion

It was found that the difference between the total cations and total anions (for imbalance) from the analysis of two brine samples, Brine 1 and Brine 2, were 5.8% and 6.3% respectively. The brines were also very dilute, with a dissolved solid content of 29.77 g/ℓ for Brine 1 and 31.26 g/ℓ for Brine 2. The conclusion to this is that the ion imbalances were so small as to be considered negligible.

The thermodynamic modelling software was able to predict and simulate the phase equilibria of a multicomponent aqueous system over a wide temperature range by estimating the standard state terms and the excess terms with the use of various thermodynamic models. This was an important step because the identities of the potential salts, the temperatures at which they would crystallise and the potential yields of the various products could be predicted before any experiments were conducted.

The thermodynamic modelling predicted that the brine samples were saturated with respect to $CaSO_4 \cdot 2H_2O$. The modelling also predicted that ice, $Na_2SO_4 \cdot 10H_20$ as well as $K_2SO_4 \cdot CaSO_4 \cdot 1H_2O$ would crystallise in a narrow temperature range from -0.8°C to -2.2°C. The thermodynamic results also showed that a high overall ion recovery (85% for Brine 1 and 71% for Brine 2) would be obtained at an operating temperature of -5°C.

However, the thermodynamics only offered an equilibrium prediction. It was only by investigating the kinetic aspects of the system that the identify, crystallisation temperatures and yield of products under real operating conditions could be confirmed.

The experiments for the kinetic phase focused primarily on the sequential removal of pure salts from a single brine under EFC conditions. The experimental work showed that relatively pure calcium sulphate (98% purity), sodium sulphate (96.4% purity) and potable water (ice) could be formed with a brine mass reduction of around 97%.

The problem with the brines initially being saturated with respect to calcium sulphate was also solved by successfully removing calcium sulphate and ice under EFC conditions. This meant that pure sodium sulphate and ice could be removed in the subsequent stage.

The validity of using synthetic versus real brines for experimental studies was established. The criterion for testing the validity was that the conductivity, pH, density measurements and ion imbalance were similar. The research showed that synthetic brine resulted in the same ice and salt nucleation temperatures as real brine and therefore could be substituted for real brine for the purposes of experimental work.

Impurity incorporation was investigated using the third brine: a platinum industry brine. It was found that the sodium sulphate crystals formed from the brine were relatively pure, but had a small quantity of selenium as an impurity incorporated in the crystal product due to isomorphic substitution. The form of the selenium was identified as selenite.

It was found that the purity of ice could be improved by adopting agitation in a vessel with a larger surface area together with washing of the final ice product. The agitation of the ice bulk resulted in the release of trapped salt, and thus an improved ice purity, while washing and removing any entrained brine on the surface of the ice crystals.

From a fundamental point of view, the mechanisms that characterise ice crystal growth include heat and mass diffusion and, depending on how they interact with each other, they affect crystal growth, morphology and ultimately the purity of ice.

In terms of yield and purity in an EFC process, the system is dependent on temperature and must be analysed on a case-by-case basis. Thermodynamic modelling was used to identify prominent features of a brine system, in particular the eutectic temperature.

A fourth brine, an alkaline sodium carbonate brine, was used to study the effects of operating temperature on yield and purity of the salt formed in the EFC process. In the sodium carbonate system, high yields of salt were observed above to its eutectic point. Ice yields increased substantially at sub-eutectic temperatures.

The concentration of impurities in the sodium carbonate decahydrate salt was found to be low, indicating a highly pure compound affected largely by entrained impurities, and not liquid inclusions or isomorphous incorporations.

Conclusion

This project has shown proof of concept of EFC as a feasible treatment for multi-component hypersaline brines. It has been shown that thermodynamic modelling can accurately predict the identifies of the recovered salts, as well as their recovery temperatures. Also, it has been showed that EFC can be used to recover multiple salts from multicomponent brines. Lastly, the study has shown that EFC can produce relatively pure salts as well as pure ice.

Further reading:
To order the report, *Extended investigations into recovery of water and salts from multi-component hypersaline brines using eutectic freeze crystallisation* (**Report No. 2012/1/13)** contact Publications at Tel: (012) 330-0340, Email: orders@wrc.org.za or Visit: www.wrc.org.za to download a free copy.