Crystallization of sodium perrhenate from NaReO$_4$–H$_2$O–C$_2$H$_5$OH solutions at 298 K

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ABSTRACT

Crystallization of sodium perrhenate (NaReO$_4$) from aqueous solution was studied by means of laboratory scale experiments at 298 K. NaReO$_4$ has a very high solubility in aqueous solution (>1130 g/L at 298 K) so crystallization was induced by the addition of ethanol (drowning-out crystallization process). This resulted in well crystalline NaReO$_4$ particles which required less energy and water than the conventional evaporative crystallization industrial process. The crystallization of NaReO$_4$ took 5–10 min and could be achieved in 1 or 2 stages by controlling the solution super-saturation by the addition of ethanol in the 25–75 vol.% range. The ethanol in solution could be recovered by distillation and recycled.

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1. Introduction

Rhenium (Re) is a rare transition metal present in nature in very low concentration (0.4 mg/t), the only commercial recovery is from molybdenite in which the rhenium occurs as a lattice substitute at 20–3000 g/t. Rhenium is being increasingly used in industry (Lipmann 2011), especially in high performance alloys for aerospace application. The element itself can be employed as a protective coating on metals, it can be alloyed with other metals to form acid- and heat-resistant materials, and it is also used for electrical and electronic filaments, electric contacts, heaters and thermocouples, due to its high melting temperature (3459 K). Rhenium compounds are used in electronic and semiconductor manufacturing; act as catalysts and as reagents in analytical chemistry and the chemical industry due to it having multiple valences (−1 to +7) (Gupta 1992; Habashi 1998; IMOA 2011; Sutulov 1980).

Rhenium is industrially produced after a series of concentration and refining operations. The main compound produced is ammonium perrhenate (NH$_4$ReO$_4$), which is synthesized from the leach solutions from primary copper, molybdenum and lead production and from solutions resulting from the recycling of rhenium-containing residues. In Chile, Molymet produces ammonium perrhenate (NH$_4$ReO$_4$) by purification of the ammonium solution obtained by the scrubbing of gases generated by molybdenite roasters (Gupta 1992; Habashi 1998; Sutulov 1980). Metallic rhenium is obtained from the perrhenate by a high temperature reduction using hydrogen.

Sodium perrhenate (NaReO$_4$) is produced from ammonium perrhenate (NH$_4$ReO$_4$) by an evaporative crystallization process (363–373 K), where the salt is precipitated by thermal evaporation of water which has a high energy cost (about 47 MJ/kg NaReO$_4$). The powder product generated by this process has low crystallinity, fine particle size and a variety of particle morphologies (Sepúlveda 2010). Sodium perrhenate is very soluble in water with Smith and Long (1948) reporting that the solubility increasing from 3.78 to 6.36 mol/kg H$_2$O as the temperature increased from 273 K to 323 K.

Crystallization of inorganic compounds dissolved in aqueous solution induced by the addition of alcohols and other organic compounds has been studied for a long time (Graber et al., 2008; Seidell and Linke 1958). Ethanol is a cheap reagent, with low toxicity and ready market availability. This new drowning-out crystallization process is expected to reduce energy cost and water consumption compared to the conventional evaporative process and permit reagent recycle thereby decreasing the operating cost of the crystallization process.

2. Experimental

The NaReO$_4$ reagent used in this study was synthesized by evaporating 1 L of an aqueous solution containing 60 g NH$_4$ReO$_4$ and 8.9 g NaOH at 353 ± 2 K. The synthesized compound was washed with acetone and dried at 313 K. The NH$_4$ReO$_4$ was provided by Molymet (purity 99.98%), the main impurities in ppm were: K 5; Fe 2; S<1; Ni 0.5; Mo 0.4; Ti 0.2; Li, Be, B, Mg, Al, P, V, Cr, Mn, Co, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Zr, Nb, Ag, Cd, In, Cs, Ba, Ta, W, Ti, Pb, Bi and U were each <0.1 ppm. X-ray diffraction confirmed the only product was sodium perrhenate.

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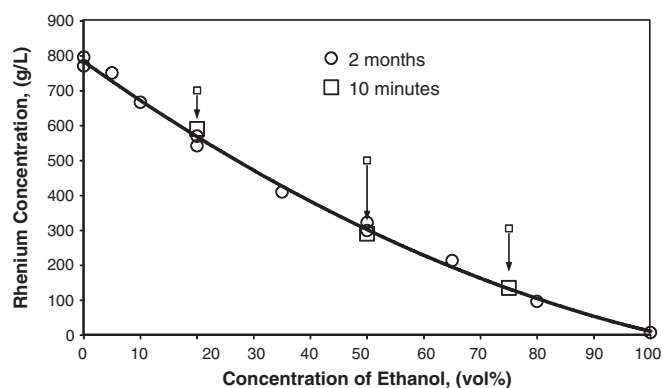 *E-mail address:* jecasas@ing.uchile.cl (J.M. Casas).

Fig. 1. Solubility of NaReO₄ in water–ethanol solutions at 298 K, the small squares are the starting compositions of the 10 min runs.

Fig. 3. Operating diagram of two crystallization stages of sodium perrhenate in H₂O–EtOH, at 298 K.

The solubility of NaReO₄ was measured in water–ethanol solutions (0, 5, 10, 20, 35, 50, 65, 80 and 100 vol.% ethanol) by immersing sealed tubes in a thermostatic water bath at 298 ± 2 K for a period of 2 months. Distilled water and 99.5% C₂H₅OH p.a. from Merck were used. The rhenium concentrations of the filtered samples were determined by ICP-OES (Perkin Elmer-Optima 5300 DV). The sodium concentrations of filtered samples were determined by atomic absorption (Perkin Elmer AAnalyst-400). The solution densities were measured using a 10 mL glass pycnometer.

Further crystallization experiments were carried out in a stirred small glass reactor in a thermostated bath (PolyScience). After 10 min residence time, the solutions were filtered through a GV 0.22 μm Millipore filter and analyzed. The collected crystals were washed with acetone and dried in an electric oven at 313 K. Then, the solid samples were homogenized and characterized by XRD, IR spectroscopy (Bruker Vector 22 spectrophotometer), SEM (JEOL JSM-5410 scanning electron microscope) and chemical analysis.

3. Results and discussion

The solubility of NaReO₄ in aqueous-ethanol solutions at 298 K are presented in Fig. 1. The solubility of perrhenate decreased markedly as the ethanol concentration increased in the solution. NaReO₄ solubility in pure water and ethanol were 1140 g/L and 20.2 g/L (equivalent to 783 g/L and 7.84 g/L of dissolved rhenium), respectively. The
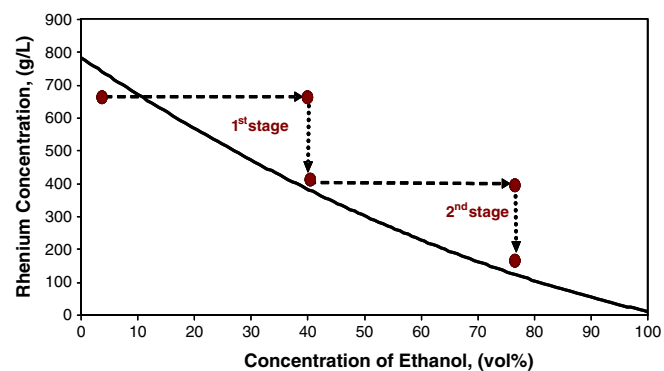
solubility of NaReO₄ was reduced by 50% in 50 vol.% ethanol and further reduced to 10% in 80 vol.% ethanol. The saturated solution densities were 1.84, 1.22 and 0.83 g/cm³ for 0, 50 and 100 vol.% ethanol respectively.

Smith and Long (1948) have shown values for sodium perrhenate solubility in water (1382 g/L), the higher value with respect to measured value of Re solubility in this study could be explain by differences in waters of hydration of the sodium perrhenates used.

Ethanol acts as co-solvent in NaReO₄–H₂O solutions and produces a decrease in the interaction forces between dissolved ions and water molecules. This generates the ionic association between ReO₄⁻ and Na⁺ species, favoring its crystallization and the consequent decrease in density and dielectric constant properties of the solution according to the Born's solubility model (Abolghassemi-Fakhree et al., 2010).

Fig. 1 also shows the results of crystallization experiments obtained after 10 min at 298 K in 20, 50 and 75 vol.% ethanol. The compositions of the analyzed solutions after 10 min of crystallization are essentially at equilibrium.

The sodium perrhenate crystals were analyzed and were of higher purity than the starting NH₄ReO₄. The carbon which was present was identified as acetone using infrared spectroscopy, this could be removed by heating the crystals.

Fig. 2 shows micrographs of sodium perrehenate crystals produced by evaporation and ethanol crystallization. The crystals formed using ethanol were larger and more crystalline than those from evaporation. The larger particle size makes the ethanol-derived product
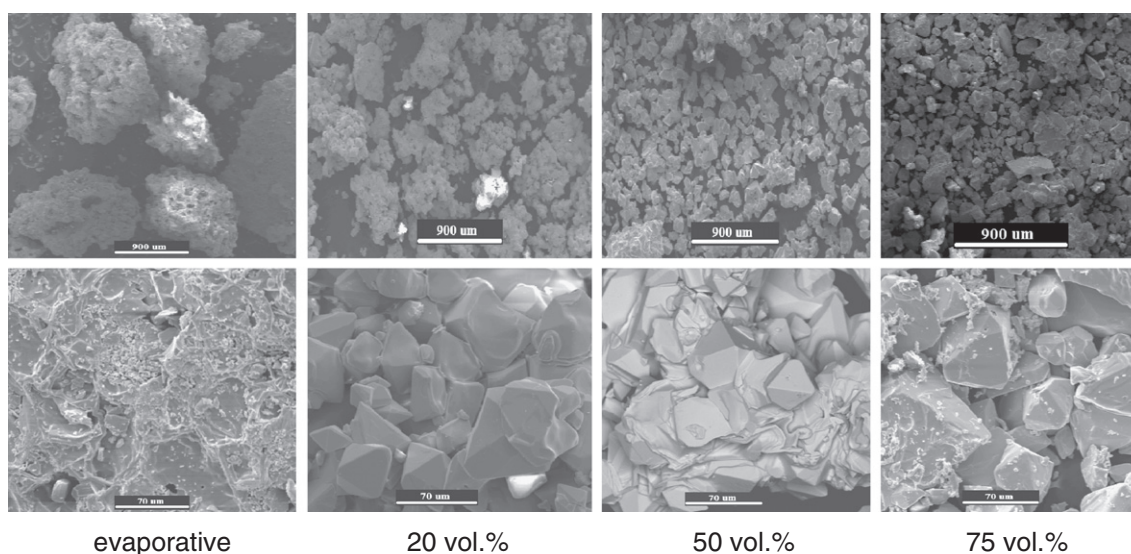

| evaporative | 20 vol.% | 50 vol.% | 75 vol.% |

Fig. 2. SEM micrographs of NaReO₄ obtained by evaporative crystallization and by crystallization at the given vol% ethanol.

Table 1
Operating cost differences between crystallization with ethanol and evaporative crystallization.

Cost Item (US$/kg NaReO$_4$)	Crystallization with ethanol	Evaporative crystallization
Power	0.58	0.96
Water	0.00	0.01
Ethanol	0.05	0.00
Total	0.63	0.97

much more amenable to solid-liquid separation. The mean particle size and extent of agglomeration both decreased as the addition of ethanol was increased. The smaller crystal size was offset by the formation of the agglomerates, giving a high particle size from all concentrations of ethanol.

From stoichiometric calculations based on the mass balances for Na and Re it was inferred that sodium perrhenate crystallized as different phases, such as: the hydrated phase NaReO$_4$·2H$_2$O in water solutions without ethanol, NaReO$_4$·H$_2$O at 20 vol.% ethanol and anhydrous NaReO$_4$ in 50 and 75 vol.% ethanol. No XRD data is available for these phases, so a positive identification cannot be made. The dehydrating properties of ethanol are well known so a decrease in waters of crystallization at high ethanol concentrations is to be expected. These results indicate that ethanol additions decreased the water activities and the crystal hydrations were dependent of the proportion of water and ethanol present in the solution.

Fig. 3 presents an operating diagram for the crystallization of sodium perrhenate from aqueous solution containing 660 g/L Re. Two crystallization stages would be required in order to obtain a product recovery of >75%. The first stage involves adding ethanol to 40 vol.% thereby decreasing the Re concentration to 410 g/L, further addition of ethanol to 75 vol.% in a second stage reduces the Re concentration to 150 g/L.

Experimental results obtained in this study help to define a conceptual process for producing sodium perrhenate by crystallization with ethanol (drowning-out crystallization process). The final ethanol aqueous solution could be distilled for recovering the ethanol and aqueous solution.

Table 1 presents a summary of operating cost differences estimated for crystallization with ethanol and evaporative crystallization. These calculations considered mass and energy balances and unitary costs of water (US$/m^3 0.4), ethanol (US$/m^3 2000), and power (US$/MWh 75).

The crystallization process with ethanol at 298 K exhibited about 35% lower operating cost in energy, ethanol and water consumptions relative to the conventional evaporative crystallization process performed at 363–373 K.

4. Conclusions

Solubility of sodium perrhenate decreased markedly as the ethanol concentration of an ethanol–water mixture increased. The measured solubilities at 298 K of NaReO$_4$ in pure water and ethanol were 1140 g/L and 20.2 g/L respectively. Ethanol was an effective co-solvent and induced the crystallization of sodium perrhenate present in aqueous solutions at room temperature.

Microscopy showed that crystal sizes of sodium perrhenate decreased as ethanol concentration increased. Mass balancing the system indicated that the waters of crystallization of the NaReO$_4$ product decreased was two at 20 vol.% ethanol. For 50 to 75 vol.% ethanol the NaReO$_4$ was anhydrous. The product had a larger particle size and more consistent morphology than the NaReO$_4$ produced by evaporation.

Finally, the proposed process for NaReO$_4$ recovery consists of 1 or 2 stages where the super-saturation is controlled by the addition of ethanol in the 25–75 vol.% range (drowning-out crystallization process). The spent ethanol-water solution obtained after separation of crystals could be distilled to recover the ethanol for recycling within the process. The more ready distillation of ethanol results in about 35% lower operating costs than the conventional evaporative crystallization method.

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