

THERMODYNAMIC ANALYSIS OF THE DEHYDRATION OF YTTRIUM AND SCANDIUM CHLORIDES

Ericksson Rocha e Almendra², Tsuneharu Ogasawara², Jorge Gomes dos Santos¹ and Flávio Teixeira da Silva²

¹IEN/CNEN Caixa Postal 2186 CEP 20001 – Ilha do Fundão, Rio de Janeiro-RJ
jg@cnen.gov.br

²COPPE/UFRJ PEMM e EE/UFRJ DEMM, Caixa Postal 68505 – Ilha do Fundão 21945-970
Rio de Janeiro-RJ, tel.: 21-2901544, fax.: 21-2906626
flatesi@metalmat.ufrj.br

ABSTRACT

The literature review shows that concentrates of light rare-earth metals, for producing the mischmetal, continues deserving efforts in the sense of improvement of the existing processes (such as fused salts electrolysis) and development of the new patented processes. With reference to the rare-earth chloride fused salts electrolysis, one critical step continues being the dehydration of the precursor chlorides. Since scandium may be present in light rare-earth minerals, dehydration of scandium chloride may be an important concern. It was found in recent studies (from 1997 to 1998) that dehydration of neodymium, lanthanum, cerium and samarium chlorides, include the use of mixed solvents (water + alcohol) in a preliminary step, followed by a thermal treatment with controlled atmosphere (pure HCl(g), or HCl(g) + argon). Dehydration of chlorides of Pr, Eu, Gd, Ho, Er, Tm, Yb and Y has been studied too. Yttrium, as an oxide or phosphate, is the main element associated to heavy rare-earth elements. Due to the importance of both elements, and as the main extraction route is by molten salt electrolysis of the chlorides, the understanding of the first step of chloride dehydration is mandatory. In order to better visualize the dehydration steps of scandium and yttrium chlorides, a thermodynamic analysis of these chlorides, evidencing the effects of temperature, water vapor pressure, hydrochloric gas pressure and inert gas pressure, is presented.

INTRODUCTION

(Bogacz et al., 1999) studied the technology of light lanthanide metals production and pointed out the following main steps:

(a) production of anhydrous lanthanide chlorides by wet or dry methods;

(b) melting of anhydrous lanthanide chlorides in a gaseous hydrogen chloride atmosphere;

(c) electrolysis of metallothermic reduction of lanthanide chlorides;

(d) recovery of rare earth chlorides from the salt after electrolysis or metallothermy, and

(e) utilization of gaseous products from the production process (chlorine, hydrogen chloride).

Thermodynamic behavior of the actinide and rare-earth chlorides in molten chlorides has been investigated by several researchers (Bechtel and Sorvick, 1999), (Hatem, 1999), (Criss and Millero, 1999), (Fukushima et al., 1997), (Fukushima et al., 1995), (Wickleder and Meyer, 1995) and (Wickleder and Meyer, 1995).

In turn, dehydration of rare-earth chlorides has been investigated in a number of studies: (Rafalski and Jonak, 1969), (Van Hong and Sundstrom, 1997) and (Kanno et al., 1998). (Van Hong and Sundstrom, 1997) investigated the dehydration of chlorides of La, Ce, Pr, Sm, Eu, Gd, Ho, Er, Tm, Yb and Y by isothermal fluidized-bed technique. By injecting a small amount of hydrochloric gas (about 1%) into the argon gas stream, hydrolysis of the chloride could be avoided.

If rare earth oxide powders are desired, then the processing of chlorides follow different routes, such as one found in the paper of (Kosynkin et al.),.

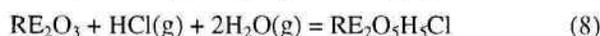
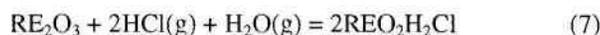
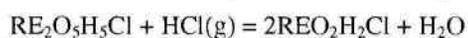
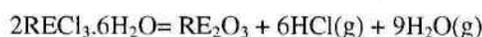
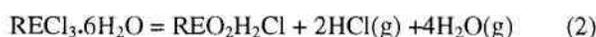
THERMODYNAMIC DATA

The thermodynamic data was found in the Main Database of the HSC Chemistry for Windows 4.0 (software licensed to the Metallurgical and Material Engineering Department of the COPPE/UFRJ).

CALCULATION AND CONSTRUCTION OF THE DIAGRAMS

The necessary thermodynamic equilibrium calculations concerning to the desired chemical reactions in the rare-earth chloride/water vapor/hydrochloric gas/inert gas system was primarily processed using the HSC software and followed by additional calculations and graphics construction and printing with the help of other softwares.

The relevant equilibrium reactions for RE = Sc or Y, are the following:



RESULTS

Figure 1 presents pHCl(g)-pH₂O(g) diagram for Sc-HCl(g)-H₂O system at 100, 200 and 300°C, which shows the following general trends:

(a) the stability domain of ScCl₃·6H₂O decreases when the temperature is raised from 100°C to 300°C, while the stability domain of the anhydrous chlorides grows correspondingly;

(b) there is always the risk of ScO₂H₂Cl scandium hydroxy-chloride formation during dehydration unless enough hydrochloric gas pressure is used;

(c) for extremely low partial pressure of the hydrochloric gas and high values of the water vapor, Sc₂O₅H₅Cl instead of ScO₂H₂Cl may form at higher temperatures (200°C and, mainly, 300°C);

(d) there isn't any possibility of Sc₂O₃ to form under low partial pressure of oxygen.

Figure 2 presents pHCl(g)-pH₂O(g) diagram for Y-HCl(g)-H₂O system at 100, 200 and 300°C, which shows the following general trends:

(e) the stability domain of YCl₃·6H₂O decreases when the temperature is raised from 100°C to 300°C, while

the stability domain of the anhydrous chlorides grows correspondingly;

(f) there is always the risk of YO₂H₂Cl yttrium hydroxy-chloride formation during dehydration unless enough hydrochloric gas pressure is used;

(g) for extremely low partial pressures of the hydrochloric gas and of the water vapor, Y₂O₃ may form instead of YO₂H₂Cl;

(h) for extremely low partial pressure of the hydrochloric gas and high of the water vapor pressure, Y₂O₅H₅Cl may form instead YO₂H₂Cl or Y₂O₃.

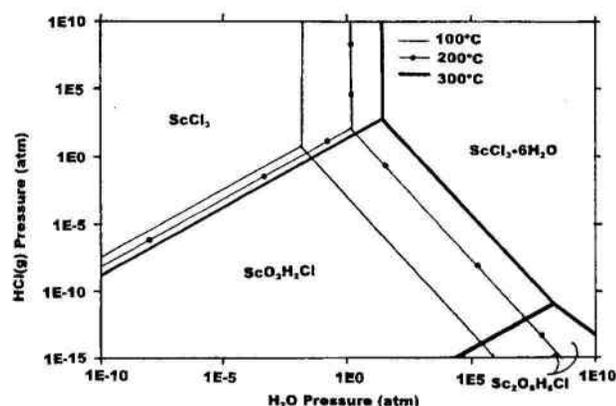


Figure 1 – pHCl(g)-pH₂O(g) diagram for Sc-HCl(g)-H₂O system at 100, 200 and 300°C

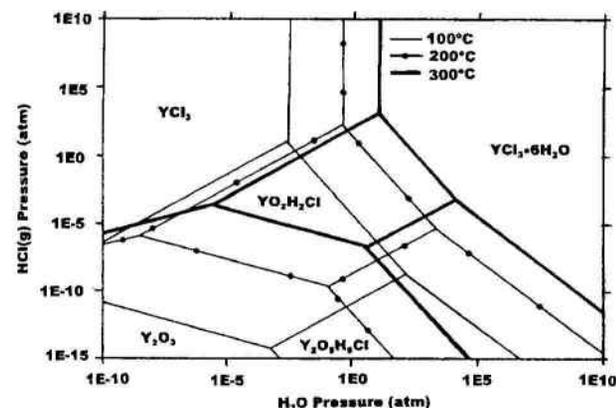


Figure 2 – pHCl(g)-pH₂O(g) diagram for Y-HCl(g)-H₂O system at 100, 200 and 300°C

DISCUSSION OF THE RESULTS

As pointed out by (Van Hong and Sundstrom, 1997), effectively the dehydration of yttrium and scandium chlorides like those of other rare-earth

chlorides are critical in the sense that tight control of the partial pressures of the hydrochloric gas and water vapor is mandatory, operating the dehydration in the appropriate temperature range (not too low such that the hydrated chloride is the stable phase, not too high to allow the formation of the anhydrous oxide).

Of course, the use of an inert gas is essential, once very low oxygen partial pressure has to be assured (in order to avoid the anhydrous oxide formation) without the need of using too much high pressure of the hydrochloric acid gas (which is considered a corrosive gas to the metallic frame of the processing plant).

Ammonium chloride may be effectively replace HCl(g) for dehydration of scandium and yttrium chlorides, once NH₄Cl decomposes during heating [see reaction (9)] and can provide the HCl(g) partial pressure required by the equilibrium reaction (5), to keep stable ScCl₃ and YCl₃ instead of ScO₂H₂Cl and YO₂H₂Cl. Unlikely, chlorine gas is unsuitable for dehydration of scandium and yttrium chlorides once the generation of HCl(g) from Cl₂(g) + H₂O(g) [see reaction (10)] is thermodynamically unfeasible at low temperatures. In order to provide the HCl(g) partial pressure required by equilibrium (5) it would need high temperatures. At these temperatures, scandium and yttrium chlorides would be decomposed in ScO₂H₂Cl and YO₂H₂Cl.

This feature will cause:

- (a) Stop the desired dehydration into anhydrous chlorides;
- (b) ScO₂H₂Cl and YO₂H₂Cl, or Sc₂O₃ and Y₂O₃ hinder the electrolytic reduction of the dehydrated chlorides in molten salts

The diagrams developed in the present work constitute a straightforward tool to safely operate the dehydration of yttrium and scandium chlorides.

CONCLUSIONS

- (a) thermodynamically favorable conditions for safe dehydration of scandium and yttrium chlorides have been established;
- (b) as the dehydration temperature is raised from 100°C to 300°C, the stability domain of the anhydrous scandium or yttrium chloride increases while that of the hydrate chloride decreases correspondingly;
- (c) ScO₂H₂Cl scandium hydroxy-chloride or YO₂H₂Cl yttrium hydroxy-chloride may form during dehydration unless enough hydrochloric gas pressure is used;

(d) Sc₂O₅H₅Cl instead of ScO₂H₂Cl may form at higher temperatures (200°C and, mainly, 300°C) when extremely low partial pressure of the hydrochloric gas and high values of the water vapor is used during dehydration;

(e) for extremely low partial pressures of the hydrochloric gas and of the water vapor, Y₂O₃ may form instead of YO₂H₂Cl;

(f) for extremely low partial pressure of the hydrochloric gas and high of the water vapor pressure, Y₂O₅H₅Cl may form instead of YO₂H₂Cl or Y₂O₃.

(g) ammonium chloride may effectively replace HCl(g) for dehydration of scandium and yttrium chlorides, but chlorine gas may not do the same due to the high temperature needed to convert Cl₂(g) in HCl(g).

ACKNOWLEDGEMENTS

The authors of the paper are grate-full to CNPq, CAPES, FINEP, FAPERJ, PADCT and CNEN for the support to this work.

REFERENCES

- Bechtel, TB, Storvick TS Activity Coefficients of Actinide and Rare-Earth Chlorides in Molten LiCl/KCl Eutectic Salt, In Industrial & Engineering Chemistry Research 38: (4) 1723, 1999.
- Bogacz, A, Rycerz L, Rumianowski S, Szymanski W, Szklarski W, Technology of Light Lanthanide Metals Production, In High Temperature Material Processes 3: (4) 461, 1999.
- Criss, CM, Millero FJ, Modeling Heat Capacities of High Valence-Type Electrolyte Solutions with Pitzer's Equations, In Journal of Solution Chemistry 28: (7) 849, 1999.
- Fukushima K, Ikumi T, Mochinaga J, Takagi R, Gauneescard M, Molar Volume Variation and Ionic Conduction in Molten ErCl₃-NaCl and ErCl₃-KCl Systems, In Journal of Alloy and Compounds 229: (2) 274, 1995.
- Fukushima K, Koseki S, Wakabayashi K, Yamane S, Iwadata Y, Molar Volume Variation and Ionic Conduction in Molten SmCl₃-NaCl, SmCl₃-KCl and SmCl₃-CaCl₂ Systems, In Journal of Alloys and Compounds 261: (1-2) 198, 1997.

- Hatem G, Semi-Empirical Dependence of the Excess Functions of Asymmetrical Molten Salt Systems, *Thermochimica Acta* 338: (1-2) 95-102, Oct. 2, 1999.
- Kanno H, Namekata S, Akama Y, Raman Study of Alcoholic Solutions of Anhydrous Rare Earth Chlorides, *Journal of Alloys and Compounds* 277: 868-871, Jul. 24, 1998.
- Kosynkin VD, Ivanov EN, Kotrekhov VA, Shtutza MG, Kardapolov AV, Grabko AI, Production of Rare Earth Polishing Powders in Russia, *Rare Earths'98*, 315-3: 179-186, 1999.
- Rafalski W, Jonak K, Investigations Dealing with Process of Dehydration Rare Earth Chlorides, *Przemysl Chemiczny* 48: (12) 735, 1969.
- Sundstrom J, Van Hong V, Investigation of the Kinetics of the Fluidized Bed Process for the Dehydration of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$, *Thermochimica Acta* 306: (1-2) 13, 1997.
- Van Hong V, Sundstrom J, The Dehydration Schemes of Rare-Earth Chlorides, *Thermochimica Acta* 307: (1) 37, 1997.
- Wickleder MS, Meyer G, Synthesis and Crystal-Structure of the Ternary Rare-Earth Chlorides Na_2MCl_5 (M = Sm, Eu, Gd), *Zeitschrift für Anorganische und Allgemeine Chemie* 621: (5) 740, 1995.
- Wickleder MS, Meyer G, Synthesis and Crystal-Structure of the Ternary Rare-Earth Chlorides NaMCl_4 (M = Eu, Yb, Y), *Zeitschrift für Anorganische und Allgemeine Chemie* 621: (4), 1995.