

**THERMODYNAMIC ANALYSIS OF THE DEHYDRATION OF LIGHT RARE-EARTH CHLORIDES***Jorge Gomes dos Santos*

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tel.: 21-2901544, fax.: 21-2906626Emails: <sup>1</sup>flatesi@metalmat.ufrj.br, <sup>2</sup>almendra@metalmat.ufrj.br, <sup>3</sup>ogasawat@metalmat.ufrj.br**ABSTRACT**

The dehydration of light rare-earth chlorides, have shown to be the critical step for the production of metal by molten salt electrolysis. From the technical literature, unfortunately in their mother language, it was shown that Russian researchers studied this problem for about 30 years ago (1969 to 1973). Recent studies (from 1997 to 1998) on dehydration of neodymium, lanthanum, cerium and samarium chlorides, have shown the use of mixed solvents (water + alcohol) in a preliminary step followed by a thermal treatment with a controlled atmosphere (HCl(g) or HCl(g) + Argon). Complementing this review, this paper presents the thermodynamic evaluation of the dehydration of light rare-earth chlorides, showing the effects of temperature, water vapor pressure, hydrochloric gas pressure and inert gas pressure.

**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) molten salt electrolysis of the lanthanide chlorides;
- (d) recovery of rare earth chlorides from the salt after electrolysis, 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., 1995) and (Wickleder and Meyer, 1995).

In turn, dehydration of rare-earth chlorides has been investigated in some number of studies (Rafalski and Jonk, 1969), (Van Hong and Sundstrom, 1997) and (Kanno, 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., 1999).

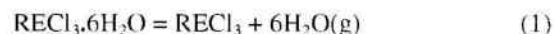
**THERMODYNAMIC DATA**

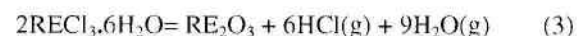
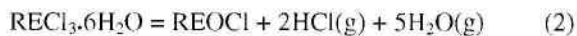
The thermodynamic data was found in the Main Database of the HSC Chemistry for Windows 4.0 (software licensed to the Metallurgical and Material Engineering Department of the COPPE/UFRJ).

**CALCULATION AND CONSTRUCTION OF THE STABILITY 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, followed by additional calculations and graphics construction with the help of other softwares.

The relevant equilibrium reactions are as follows:





### COMMENTS ON THE STABILITY DIAGRAMS

Figures 1 to 6 present the  $\text{pHCl}(\text{g})$ - $\text{pH}_2\text{O}(\text{g})$  diagrams for La, Ce, Pr, Nd, Sm, Eu and Gd at 100, 200 and 300°C, showing the following general trends:

(a) the stability domain of  $\text{RECl}_3 \cdot n\text{H}_2\text{O}$  decreases when the temperature is raised from 100°C to 300°C, while the stability domain of the anhydrous chlorides grow correspondingly;

(b) there is always the risk of rare-earth oxy-chloride formation during dehydration, unless enough hydrochloric gas pressure is used;

(c) for too low partial pressure of the hydrochloric gas (and increasingly for higher vapor pressures), rare-earth oxide instead of anhydrous chloride or oxy-chloride may form at higher temperatures (200°C and, mainly, 300°C).

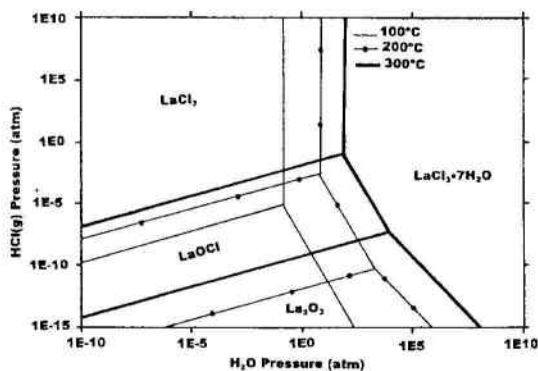


Figure 1 –  $\text{pHCl}(\text{g})$ - $\text{pH}_2\text{O}(\text{g})$  diagram for La-HCl(g)- $\text{H}_2\text{O}(\text{g})$  system at 100, 200 and 300°C

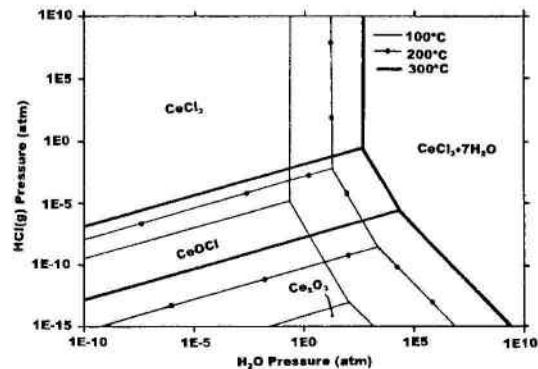


Figure 2 –  $\text{pHCl}(\text{g})$ - $\text{pH}_2\text{O}(\text{g})$  diagram for Ce-HCl(g)- $\text{H}_2\text{O}(\text{g})$  system at 100, 200 and 300°C

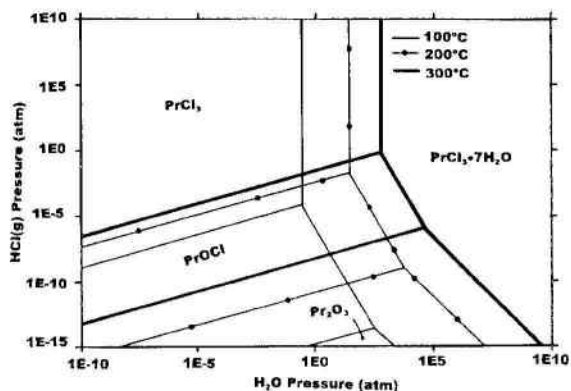


Figure 3 –  $\text{pHCl}(\text{g})$ - $\text{pH}_2\text{O}(\text{g})$  diagram for Pr-HCl(g)- $\text{H}_2\text{O}(\text{g})$  system at 100, 200 and 300°C

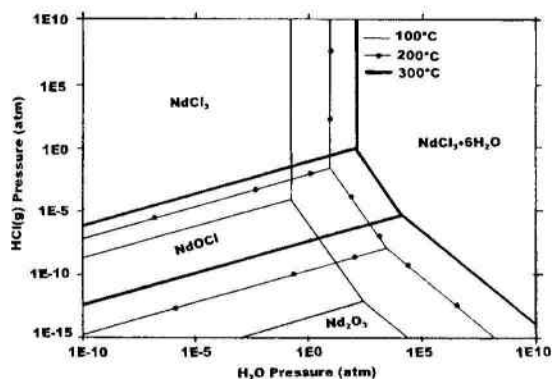


Figure 4 –  $\text{pHCl}(\text{g})$ - $\text{pH}_2\text{O}(\text{g})$  diagram for Nd-HCl(g)- $\text{H}_2\text{O}(\text{g})$  system at 100, 200 and 300°C

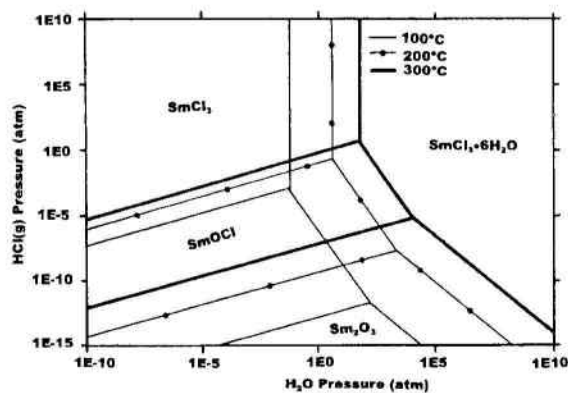


Figure 5 –  $\text{pHCl}(\text{g})$ - $\text{pH}_2\text{O}(\text{g})$  diagram for Sm-HCl(g)- $\text{H}_2\text{O}(\text{g})$  system at 100, 200 and 300°C

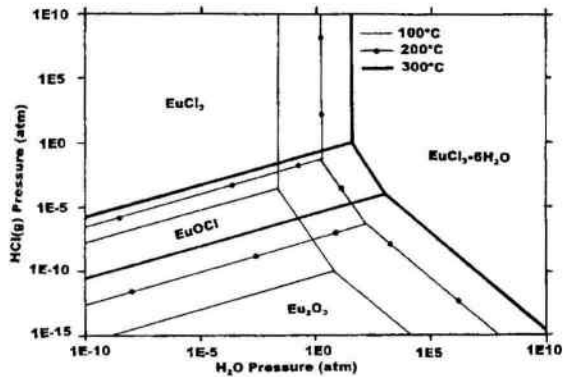


Figure 6 –  $p_{\text{HCl(g)}}-p_{\text{H}_2\text{O(g)}}$  diagram for Eu-HCl- $\text{H}_2\text{O}$  system at 100, 200 and 300°C

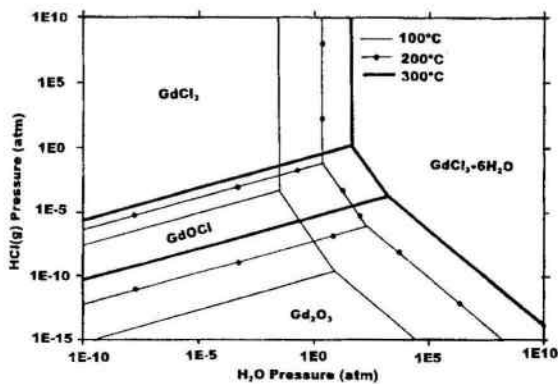


Figure 7 –  $p_{\text{HCl(g)}}-p_{\text{H}_2\text{O(g)}}$  diagram for Gd-HCl(g)- $\text{H}_2\text{O(g)}$  system at 100, 200 and 300°C

## DISCUSSION

As pointed out by (Van Hong and Sundstrom, 1997), effectively the dehydration of 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).

The following relevant point in this discussion is that concerned with the replacement of the  $\text{HCl(g)}$  by ammonium chloride. The natural question is: what will happen? The answer is: ammonium chloride will decompose into  $\text{HCl(g)}$  and

$\text{NH}_3(\text{g})$  during heating of the rare-earth metal chloride hydrate and will provide the necessary  $\text{HCl(g)}$  to avoid the decomposition of the rare-earth metal chloride into  $\text{REOCl}$  or  $\text{RE}_2\text{O}_3$ . The supply of ammonium chloride must exceed the amount capable of providing the  $\text{HCl(g)}$  pressure predicted by the equilibrium reaction (4).

The next question; is it possible to replace  $\text{HCl(g)}$  by  $\text{Cl}_2(\text{g})$ ? The answer is no, because formation of  $\text{HCl(g)}$  from  $\text{Cl}_2(\text{g}) + \text{H}_2\text{O(g)}$  is only thermodynamic feasible at very high temperatures. Therefore, rare-earth metal chlorides will decompose into oxy-chloride or oxide at low temperatures during heating in a chlorine gas atmosphere.

Finally, any thin film of rare-earth oxide or even rare-earth oxy-chloride will tend to inhibit the subsequent reduction process because reduction of oxide or oxy-chloride is thermodynamically more difficult than that of anhydrous chloride.

The diagrams developed in the present work constitute a straightforward tool to operate with confidence the dehydration of rare-earth chlorides.

## CONCLUSIONS

(a) thermodynamic conditions appropriate for safe dehydration of light rare-earth chlorides have been established;

(b) as the dehydration temperature is raised from 100°C to 300°C, the stability domain of the anhydrous rare-earth chloride increases while that of the hydrated chloride decreases correspondingly;

(c) rare-earth oxy-chloride and even rare-earth oxide may be formed during dehydration, if too low values of the hydrochloric gas pressure is used, mainly at higher pressures of water vapours and higher temperatures.

(d) ammonium chloride may replace effectively  $\text{HCl(g)}$  for dehydration of rare-earth metal chlorides. The dehydration with  $\text{Cl}_2(\text{g})$  is thermodynamic unfeasible.

## ACKNOWLEDGEMENTS

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