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THERMAL REDUCTION OF YTTRIUM OXIDE TO YTTRIUM

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1 INTRODUCTION

- The U.S. Department of energy has categorised yttrium(Y) as “critical mineral” for US economy as critical materials are essential in energy technologies and its shortage would disrupt the supply chain. Y is commonly used in LED , phosphors, electronic, ceramics and clean energy for sustainable society . So, there is demand for production of rare earth supply for US renewable industry.

- The most common industrial processes for rare earth metal production are molten salt electrolysis and metallothermic reduction . Metallothermic process involves the reduction of a rare earth compounds with a highly reactive metal to produce high purity rare earth metals.

- Metallothermic reduction is done to reduce neodymium chloride to pure neodymium(Nd) in presence of calcium and calcium fluoride as a flux to yield 100 wt.% Nd at 1000°C- **$NdCl_3 + Ca + xCaF_2 \rightarrow Nd + CaCl_3 + xCaF_2$** .Chiou et al.(1998)

- Further,NdF_3 (Velu and Reddy,2005) is reduced to Nd using Ca and $CaCl_2$ at 1000°C to yield 100 wt.% Nd metal.-**$2NdF_3 + 3Ca+xCaCl_2 \rightarrow 2Nd + 3CaF_2 + xCaCl_2$**

- In this study, thermodynamic analysis of reduction of yttrium oxides/halides to yttrium using reactive reductants (Li, Ca, K, Na) was investigated. A process flowsheet was developed for production of high purity yttrium.

2 METHODS

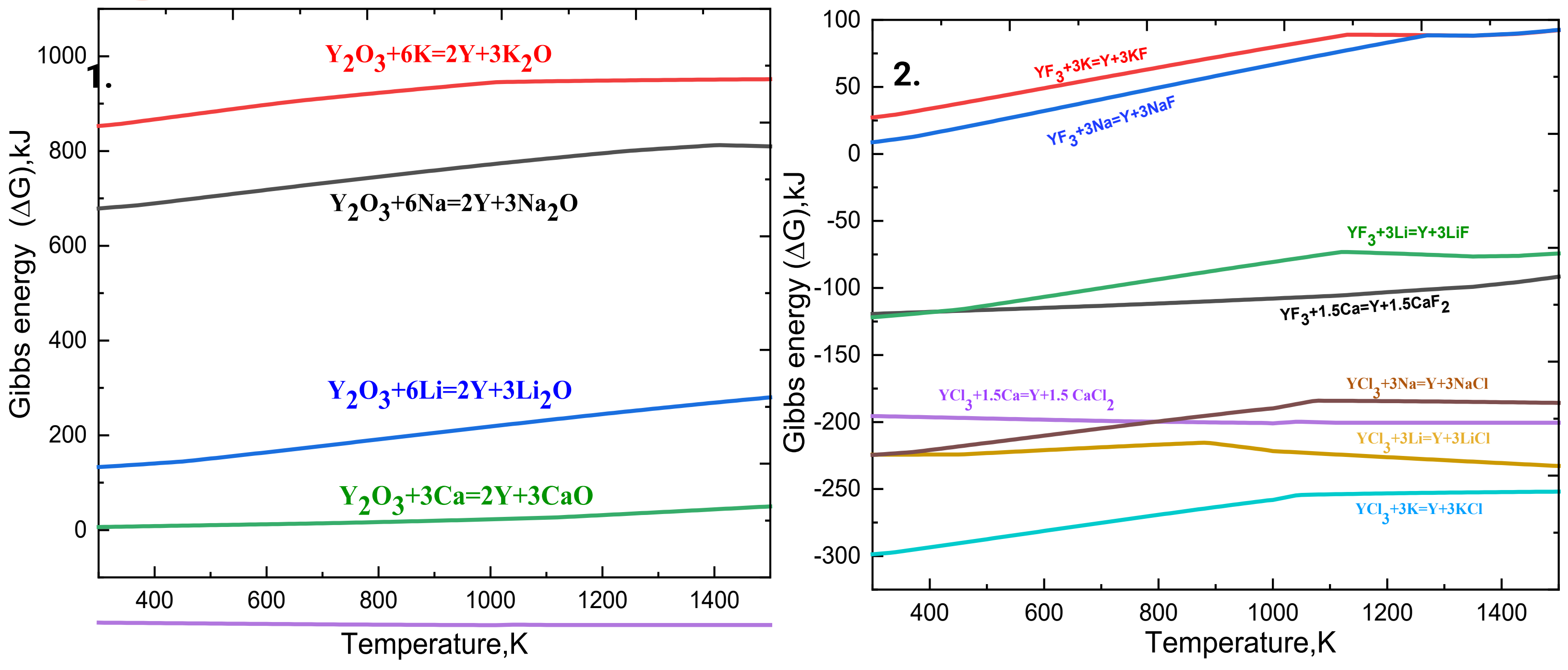


Fig 1- Gibbs energy change as a function of temperature for reduction of yttrium oxides/halides

- **Gibbs energy minimization method is one way modelling of phase equilibria where at equilibrium, the total Gibbs energy of the system has minimum value. The reaction will proceed left to right if ,$\Delta G_r = \Delta G_{product} - \Delta G_{reactant}$ is negative.**

- Using the “reaction” module of HSC software, the change in Gibbs energy of the redox reactions were calculated. Fig 1 shows that Y_2O_3 cannot be reduced to Y due to positive Gibbs energy of the reaction.For YF_3 and YCl_3 ,the negative change in Gibbs energy values suggest the reactions are exergonic i. e. , spontaneous in forward direction.

- Therefore, the electro-reduction of yttrium halides was thermodynamically favored when calcium and lithium was added as reactant.

3 RESULTS

- **Reduction of YCl_3 to Y**

1) $1/3Y_2O_3+C+Cl_2 \xrightarrow{650°C} 2/3YCl_3+ CO$
2) $YCl_3 + 3Li \xrightarrow{1000°C} Y\text{ (crystal)} + 3LiCl\text{ (g)}$
3) $2YCl_3 + 3Ca \xrightarrow{1350°C} 2Y + 3CaCl_2$

- **Reduction of YF_3 to Y**

1) $Y_2O_3+6NH_4HF_2 \xrightarrow{300°C} 2YF_3 + 6NH_4F + 3H_2O$
2) $2YF_3+3Ca + xCaCl_2 \xrightarrow{1300°C} 3CaF_2+2Y+ xCaCl_2$

Y yield was higher when YCl_3 reacts with Li as shown in Fig 2

During chlorination process, carbon helps to reduce the potential of 0_2 and favor formation of pure YCl_3.Nolting et al.(1960) investigated the formation of high purity yttrium by reaction of YCl_3 and Li at 1000°C by bomb reduction. The by-product LiCl was removed by distillation process.

A high yield yttrium (98 wt.%) was obtained by adding sufficient $CaCl_2$ to YF_3 and Ca mixture.-Daane and Spedding (1952)

The Gibbs energy of formation should be sufficiently high to ensure a greater reduction of metal. At equilibrium,YCl_3 has a higher negative Gibbs energy value as compared to YF_3 which increases the yield of yttrium to 99.8 wt.%.

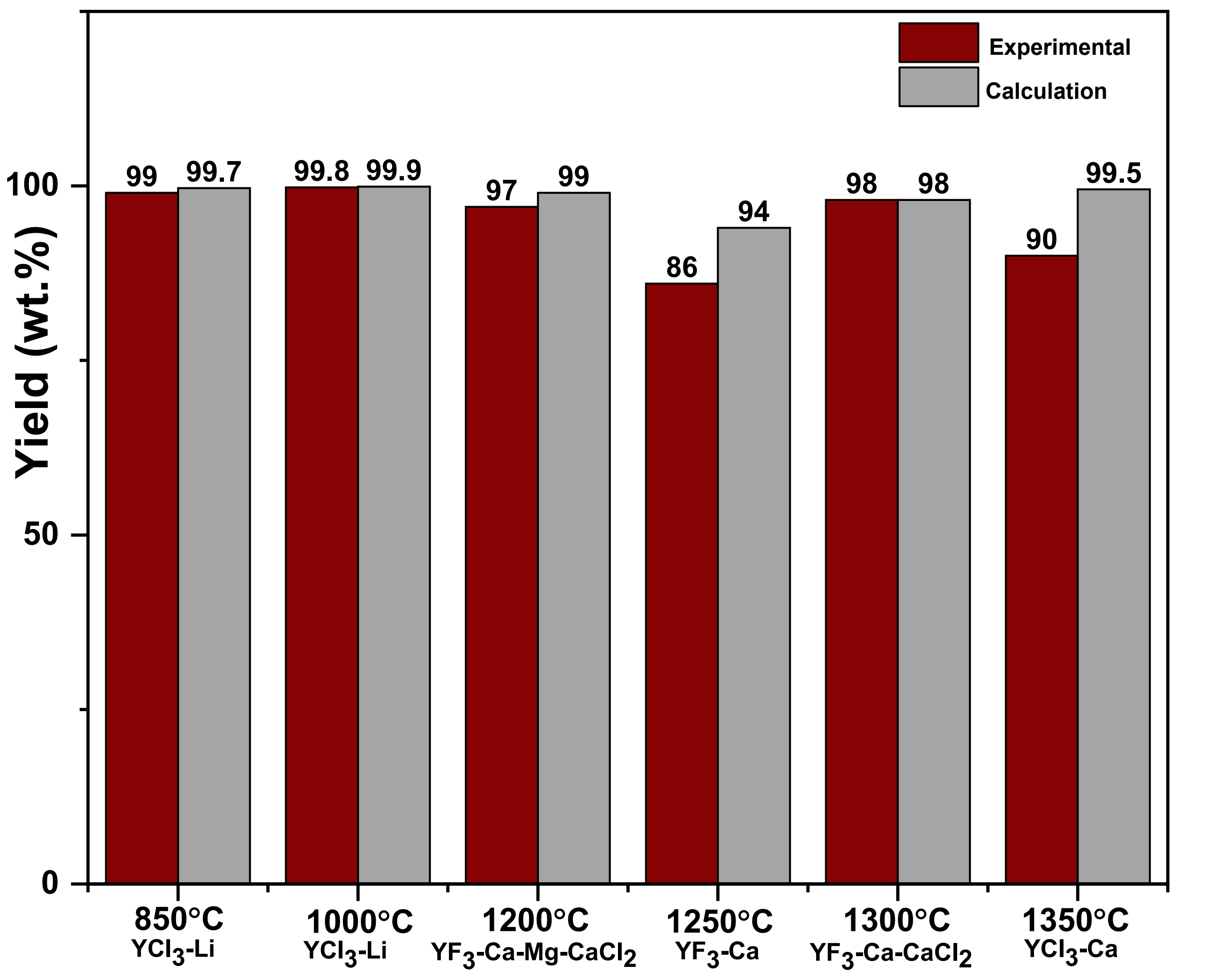


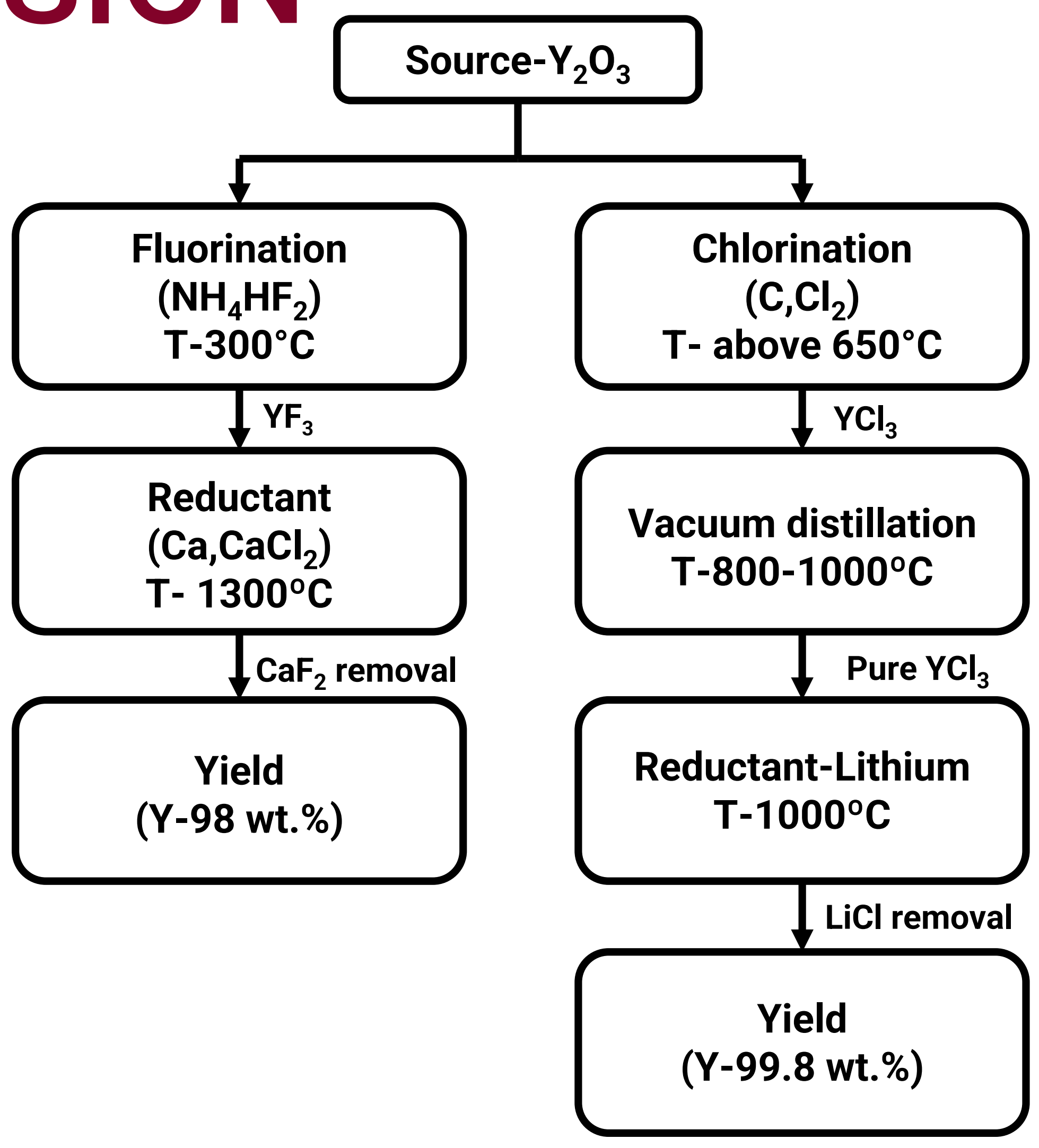
Fig 2- Variation of yttrium yield depending on differentYCl_3 and YF_3 system.

4 DISCUSSION

Fig 2 shows the variation of the percentage yield of Y when all the systems are kept at 1 atm. The YCl_3 –Li system shows the highest Y yield of 99.8% and has good agreement between calculated and experimental data .

For fluorides, YF_3-Ca-$CaCl_2$ system was the most efficient process with Y yield of 98%.The experimental and calculated values were the same.

Taking all parameters into consideration, a process flowsheet was developed to produce high purity yttrium metal from its respective halides.(Fig 3)


Source-Y_2O_3

Fluorination (NH_4HF_2) T-300°C
YF_3
Reductant ($Ca,CaCl_2$) T- 1300°C
CaF_2 removal
Yield (Y-98 wt.%)

Chlorination (C,Cl_2) T- above 650°C
YCl_3
Vacuum distillation T-800-1000°C
Pure YCl_3
Reductant-Lithium T-1000°C
LiCl removal
Yield (Y-99.8 wt.%)

Fig 3-Flowsheet to produce high purity yttrium metal (T= temperature)

5 CONCLUSIONS

- In metallurgical process, the feasibility of reactions was studied by Gibbs energy diagrams . The change in Gibbs energy of the reduction reactions between yttrium oxides/halides and the reductants (K, Li, Na and Ca) was calculated between 300-1500K.In the present system, calcium and lithium were the active species for the reduction of yttrium halides.

- For yttrium extraction, yttrium oxide was fluorinated to YF_3 by reaction with ammonium bifluoride . The metallic reduction of YF_3 to Y was done at 1300ºC using calcium as reductant and calcium chloride as flux material to lower the melting point of slag. The yttrium yield was 98 wt.%.

- Further, the yttrium yield was increased to 99.8 wt.% when yttrium chloride was reduced by lithium metal at a lower temperature of 1000ºC.The chlorination of Y_2O_3 to YCl_3 was done by reaction with carbon and chlorine.

REFERENCES

▪Block, F E,1964. Preparation of yttrium and rare earth metals by metallothermic reduction, thesis, Oregon state university, Oregon.
▪Bogala, M. R., & Reddy, R. G.,2016. Thermodynamic assessment of tio2 reduction to TI Metal in molten cacl2. Journal for Manufacturing Science and Production, 16(1), 1–11. https://doi.org/10.1515/jmsp-2016-0003
▪Carlson, O.N., Schmidt, F.A., and Spedding, F.H. ,1956. Preparation of yttrium metal by reduction of yttrium trifluoride with calcium, Report ISC-744, U.S. Atomic Energy Commission, National Technical Information Service, Springfield, Virginia.
▪Daane, A. H., & Spedding, F. H. (1952). The Preparation of Yttrium and Some Heavy Rare Earth Metals. https://doi.org/10.2172/4385900
▪Haefling, J.A., Schmidt, F.A., and Carlson, O.N. ,1961. A study of several metals as reductants for yttrium fluoride, Research and Development Report ISC-374, Ames Laboratory, USAEC, National Technical Information Service, Springfield Virginia.
▪Nolting, H. J., Simmons, C. R., & Klingenberg, J. J. ,196). Preparation and properties of high purity yttrium metal. Journal of Inorganic and Nuclear Chemistry, 14(3–4), 208–216. https://doi.org/10.1016/0022-1902(60)80260-6
▪P. T. Velu and R. G. Reddy,2005. “Calciothermic Reduction of Neodymium Fluoride”, Light Metals 2005, ed. Halvor Kvande, TMS, Warrendale, USA, pp 1155-1159
▪R. S. Chiou, P. T. Velu, and R. G. Reddy ,1998. “Thermodynamic Modeling of Calciothermic Reduction of NdCl3,” Light Metals, ed. by B. Welch, TMS, pp. 1327-1331