From Metals Chemistry to Materials Science: was something left out?

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	I	II	PERIODIC TABLE										III	IV	V	VI	VII	VIII
1	H_1		**Biomaterials Revolution**															He_2
2	Li_3	Be_4											B_5	C_6	N_7	O_8	F_9	Ne_{10}
3	Na_{11}	Mg_{12}											Al_{13}	Si_{14}	P_{15}	S_{16}	Cl_{17}	Ar_{18}
4	K_{19}	Ca_{20}	Sc_{21}	Ti_{22}	V_{23}	Cr_{24}	Mn_{25}	Fe_{26}	Co_{27}	Ni_{28}	Cu_{29}	Zn_{30}	Ga_{31}	Ge_{32}	As_{33}	Se_{34}	Br_{35}	Kr_{36}
5	Rb_{37}	Sr_{38}	Y_{39}	Zr_{40}	Nb_{41}	Mo_{42}	Tc_{43}	Ru_{44}	Rh_{45}	Pd_{46}	Ag_{47}	Cd_{48}	In_{49}	Sn_{50}	Sb_{51}	Te_{52}	I_{53}	Xe_{54}
6	Cs_{55}	Ba_{56}	La_{57}	Hf_{72}	Ta_{73}	W_{74}	Re_{75}	Os_{76}	Ir_{77}	Pt_{78}	Au_{79}	Hg_{80}	Tl_{81}	Pb_{82}	Bi_{83}	Po_{84}	At_{85}	Rn_{86}
7	Fr_{87}	Ra_{88}	Ac_{89}	Rf_{104}	Db_{105}	Sg_{106}	Bh_{107}	Hs_{108}	Mt_{109}	Ds_{110}	Rg_{111}	Uub_{112}	Uut_{113}	Uuq_{114}	UUp_{115}	Uuh_{116}	Uus_{117}	Uuo_{118}

Ce_{58}	Pr_{59}	Nd_{60}	Pm_{61}	Sm_{62}	Eu_{63}	Gd_{64}	Tb_{65}	Dy_{66}	Ho_{67}	Er_{68}	Tm_{69}	Yb_{70}	Lu_{71}
Th_{90}	Pa_{91}	U_{92}	Np_{93}	Pu_{94}	Am_{95}	Cm_{96}	Bk_{97}	Cf_{98}	Es_{99}	Fm_{100}	Md_{101}	No_{102}	Lr_{103}

Expansion of Programs

- Biomaterials
- Electronic materials

- No appreciable addition of faculty
- No much additional resources

- Something is left out: Less in depth coverage
- Very little organic chemistry in curriculum
- No much interdisciplinary approach in subjects

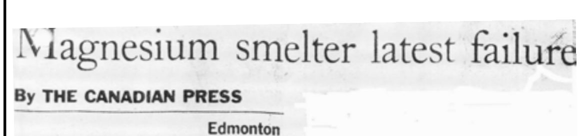
- Life-long learning

Sustainable Production Requires Sustainable Knowledge

University: A place to learn

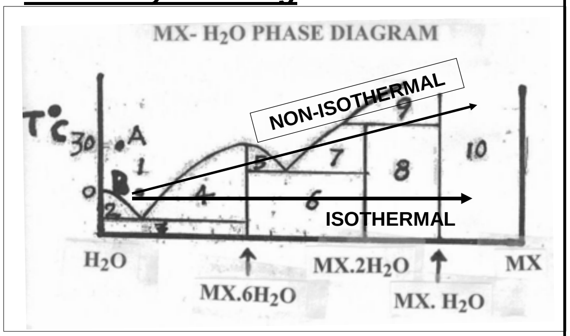
Sustainable Production Requires Sustainable Knowledge

University: A place to think



Example 1: Dehydration

University teaching



Example 1: Dehydration

MIT-General Motors-TUNS period

- **Molten salts process development and design**
- **From lab to industry scale-up**
- **Technology evaluation**

•Magnesium

•Neodymium

Objective

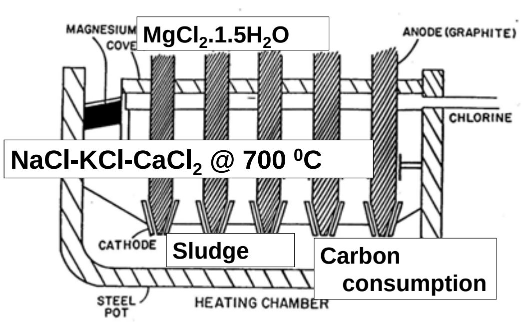
To demonstrate the importance of knowing the water/oxide content in the electrolysis feed of reactive metals.

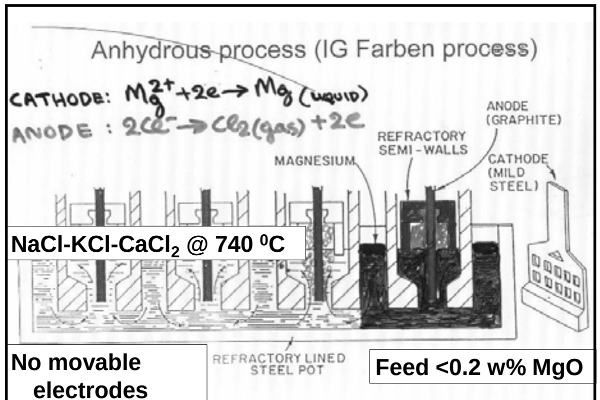
Examples: neodymium and magnesium

Is water in molten salt bad?

It depends…

Dow Chemical Magnesium Cell (Hydrous Process)





Is water in molten salts bad?

Yes, if water is not expected to be there

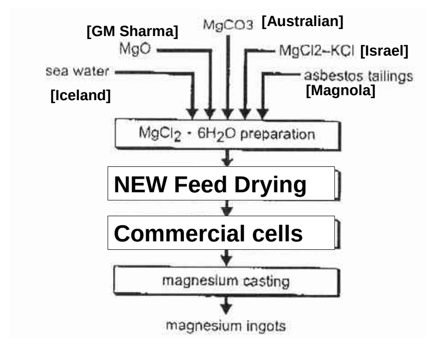
MAGNESIUM PRODUCTION PROPOSED PROCESSES

- **Australian magnesium (QMC) (Alcan multi- polar cells)**
- **Icelandic Magnesium (similar to Dow/ carnalite)**
- **Magnola Metallurgy (Alcan multi-polar cells)**
- **Dead Sea (Carnalite Russian cell)**
- **GM/Sharma**

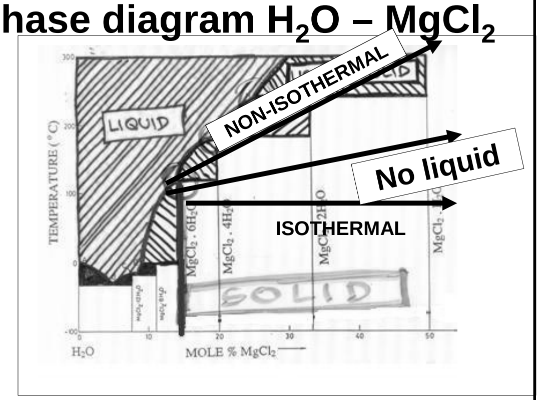
Magnesium Sources

MAGNESIUM SOURCES AND CONCENTRATIONS		
Source	Formula	% MG
Sea Water	$MgCl_2 \bullet\bullet MgSO_4$	0.14%
Lake Brine	$MgCl_2 \bullet\bullet MgSO_4$	0.80%
Carnallite	MgCl•KCl•6H2O	8.80%
Dolomite	$MgCO_3 \bullet CaCO_3$	13.20%
Serpentine	$3MgO \bullet 2SiO_2 \bullet 2H20$	26.40%
Magnesite	$MgCO_3$	28.83%

Mg proposed new processes



Phase diagram H_2O – $MgCl_2$



Relevant publications

- **G.J. Kipouros and D.R. Sadoway, "The Chemistry and Electrochemistry of Magnesium Production" in Advances in Molten Salt Chemistry, Vol. 6, Edited by G. Mamantov et al., Elsevier, Amsterdam, pp. 127-209 (1987).**
- **G.J. Kipouros and D.R. Sadoway, "A thermochemical analysis of the production of $MgCl_2$", Journal of Light Metals, 1 (2), 111-117 (2001).**

DEHYDRATION REACTIONS –FIRST STEPS

$MgCl_2*6H_20_{(s)} = MgCl_2*4H_20_{(s)} + 2H_20(v)$	
$MgCl_2*4H_20_{(s)} = MgCl_2*2H_20_{(s)} + 2H_20(v)$	
$MgC1_2* 2H_20_{(s)} = MgCl_2*H_20_{(s)} + H_20(v)$	

HYDROLYSES REACTIONS

$MgCl_{2*}2H_20_{(s)} = MgOHCl_{(s)} + HCl(g) + H_20(v)$	
$MgCl_{2\,(s)} + H_20(v) = MgOHCl_{(s)} + HCl(g)$	
$MgCl_2*H_20_{(s)} = MgOHCl_{(s)} + HCl(g)$	
$Mg0HCl = MgOH^+ + Cl^-$	MELTING
$MgOHCl = MgO_{(s)} + HCl(g)$	OXIDE FORMATION

DEHYDRATION REACTIONS –FINAL STEP

$$MgCl_2*H_20_{(s)} = MgCl_{2(s)} + H_20(v)$$

HYDROXYCHLORIDES HYDRATES

$MgClOH$	$Mg_3Cl(OH)_5.4H_2O$
$Mg_2(OH)_3Cl$	$Mg_3(OH)_5Cl.4H_2O$
$MgOHCl$	$Mg_2(OH)_3Cl.2H_2O$
$Mg(OH)Cl$	$Mg_3(OH)_5$ Cl.3H2O
$Mg_2Cl(OH)_3$	$Mg_2(OH)_3Cl.4H_2O$
$Mg_2Cl(OH)_3.4H_2O$	$Mg_{10}(OH)_{18}Cl.5H_2O$
$Mg_3Cl_2(OH)_4.2H_2O$	$Mg_2(OH)_3Cl.3H_2O$
$Mg_{10}Cl_2(OH)_{18}.5H_2O$	

DEHYDRATION

$MgCl_2.6H_20_{(s)} = MgCl_2.4H_20_{(s)} + 2H_20(g)$ (1)

$K_1 = P^2_{H2O}*a_{MgCl2.4H20} / a_{MgCl2.6H20}$ (2)

ASSUMPTIONS:

a.Hydrates are solids

b.Hydrates are mutually insoluble

$a_{MgCl2.4H20} = 1$

$a_{MgCl2.6H20} = 1$

$K_1 = P^2_{H2O}$

$\Delta G^0_1 = -RTlnK_1 = -2RTlnP_{H20}$

$\Delta G^0_1 = ???$

For the reaction

$MgCl_2*6H_20_{(s)} = MgCl_2*4H_20_{(s)} + 2H_20(v)$

$K = P^2_{H2O}$

$\Delta G^0 = -RTlnK = -2RTlnP_{H20}$

and

$\log P_{H20} = 6.335 - 0.608x10^{-3} T + 0.42llogT - 3{,}039T^{-l}$

DEHYDRATION

$MgCl_2.6H_20 = MgCl_2.4H_20 + 2H_20(g)$ (1)

Temperature range 298-390 K, where the hexahydrate is stable.

$K_1 = lnP^2_{H2O}*a_{MgCl2.4H20} / a_{MgCl2.6H20}$ (2)

$\Delta G^0_1 = -RTlnK_1 = -2RTlnP_{H20} - RTln\ a_{MgCl2.4H20} + RTln\ a_{MgCl2.6H20}$ (3)

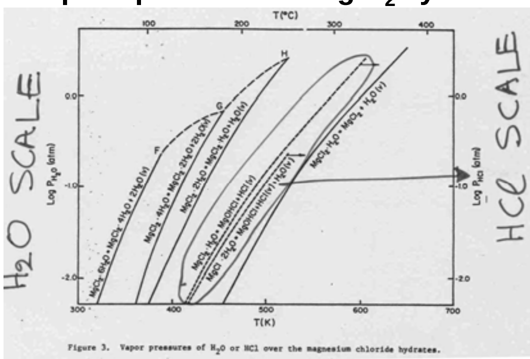
A knowledge of activities is needed to use (3). For example:

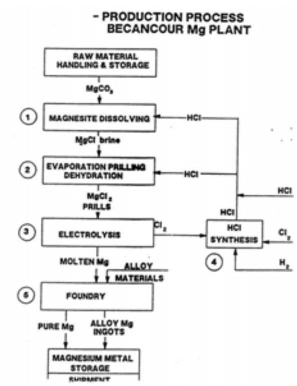
$a_{MgCl2.4H20} / a_{MgCl2.6H20} = 0.01$

the vapour pressure is changed by a factor of 100 compared to the situation in which there is no liquid phase.

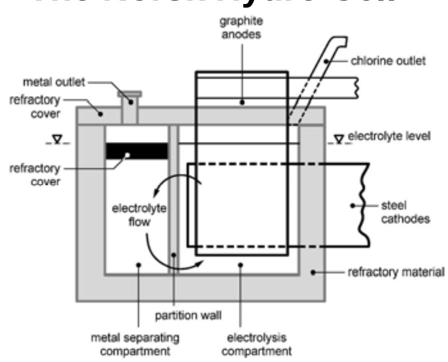
DEHYDRATION AND HYDROLYSIS REACTIONS		
DEHYDRATION REACTIONS –FIRST STEPS		
$MgCl_2*6H_20_{(s)} = MgCl_2*4H_20_{(s)} + 2H_20(v)$	$K_1 = P^2_{H2O}$	$\log P_{H20} = 6.335 - 0.608x10^{-3} T + 0.42llogT - 3{,}039T^{-l}$
$MgCl2*4H20_{(s)} = MgCl_2*2H_20_{(s)} + 2H_20(v)$	$K = P^2_{H2O}$	$logP^2_{H2O} = 8.248 - O.608x10^{-3} T + O.O75logT - 3{,}605T^{-l}$
$MgC1_2* 2H_20_{(s)} = MgCl_2*H_20_{(s)} + H_20(v)$	$K = P_{H2O}$	$logP_{H2O} = 9.242 - O.608xl0^{-3}T - O.428logT - 3.833T^{-1}$
HYDROLYSIS REACTIONS		
$MgCl_{2*}2H_20_{(s)} = MgOHCl_{(s)} + HCl(g) + H_20(v)$	$K = P_{H2O}*P_{HCl}$	$logP_{H2O} P_{HCl} = 18.866 - l.060x10^{-3} T - l.259logT - 7{,}895T$
$MgCl_{2\,(s)} + H_20(v) = MgOHCl_{(s)} + HCl(g)$	$K = P_{HCl} / P_{H2O}$	
$MgCl2*H20_{(s)} = MgOHCl_{(s)} + HCl(g)$	$K = P_{HCl}$	$Log\ P_{HCl} = 9.633 - 0.452x10^{-3}T - 0.83OlogT - 4.042T^{-1}$
DECOMPOSITION UPON MELTING		
$Mg0HCl = MgOH^+ + Cl^-$		
OXIDE FORMATION		
$MgOHCl = MgO_{(s)} + HCl(g)$	$K = P_{HCl}$	$\log P_{HCl} = 1.309 - 0.228x10^5T^{-2} - l.359x10^{-3} T + 2.094 logT - 5{,}181T^{-1}$
DEHYDRATION REACTIONS –FINAL STEP		
$MgCl_2*H_20_{(s)} = MgCl_{2(s)} + H_20(v)$	$K = P_{H2O}$	$\log P_{H2O} = 9.049 - 0.608x10^{-3}T - 0.452logT - 4.471T^{-1}$

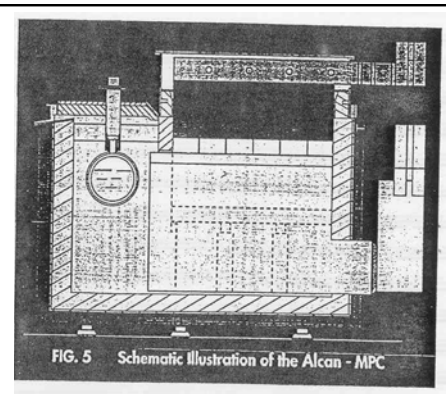
Vapour pressure of $MgCl_2$ hydrates



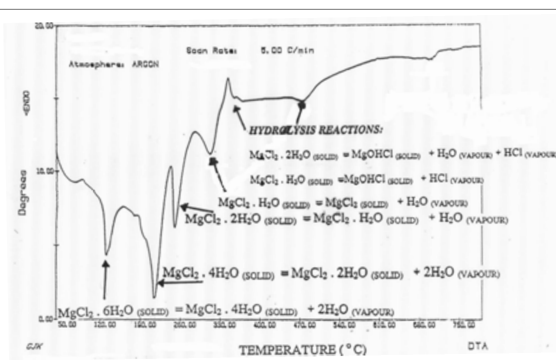


The Norsk Hydro Cell

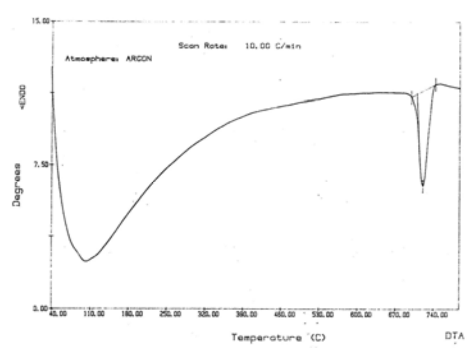




DTA of $MgCl_2.6H_2O$



DTA of pure anhydrous $MgCl_2$



Analytical chemistry

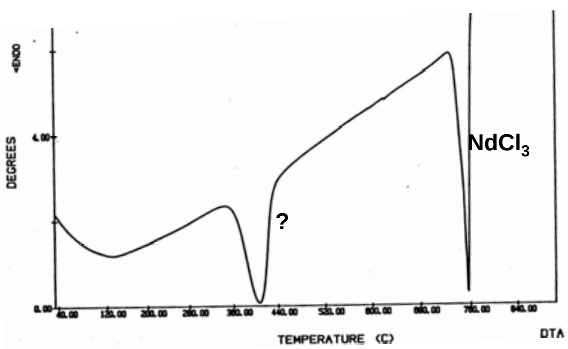
Industry prefers:

- **One technique to give the answer to water and oxygen content of the electrolysis feed.**

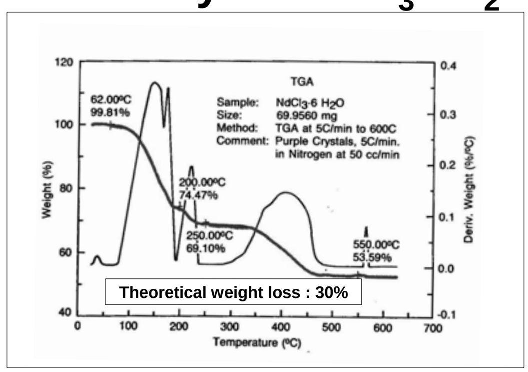
- **Unfortunately the proposed processes were designed relying on a semi-quantitative oxide speciation analytical technique. It is based on HCl titration of oxide and hydroxychloride.**

The $NdCl_3.6H_2O$ paradigm

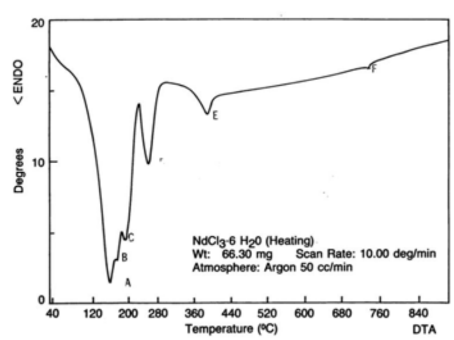
DTA Anhydrous commercial pure $NdCl_3$



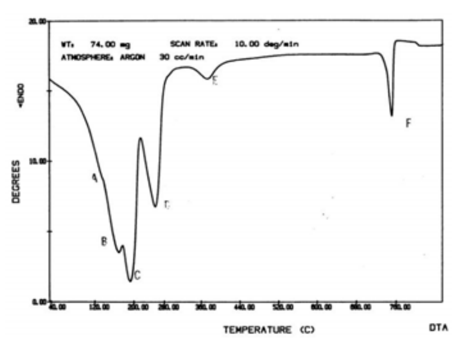
TGA analysis $NdCl_3.6H_2O$



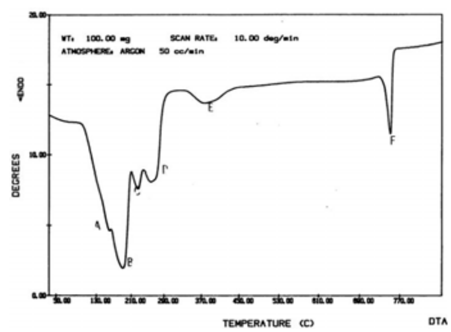
DTA $NdCl_3.6H_2O$



$NdCl_3.6H_2O$ Dehydration 1

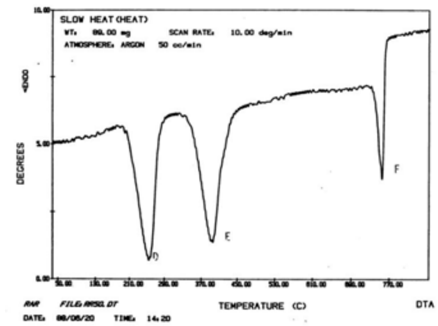


$NdCl_3.6H_2O$ Dehydration 2



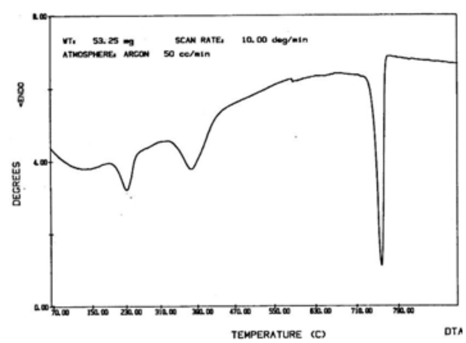
Was something left out ? 4th Workshop on Reactive Metals Processing, MIT 2008

$NdCl_3.6H_2O$ Dehydration 3



Was something left out ? 4th Workshop on Reactive Metals Processing, MIT 2008

$NdCl_3.6H_2O$ Dehydration 4



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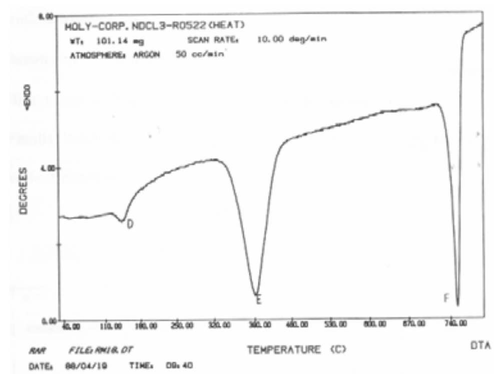

Fig. 8. DTA curve of batch 1.

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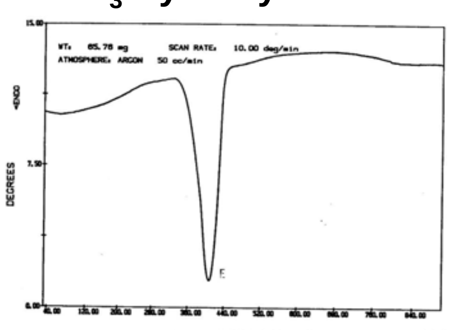
$NdCl_3$ Hydroxychloride



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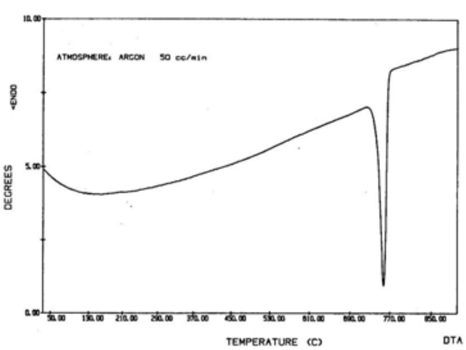
$NdCl_3$ Anhydrous



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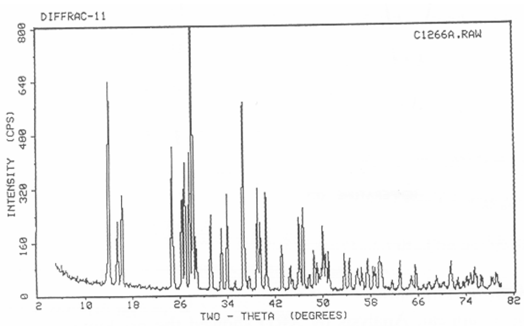
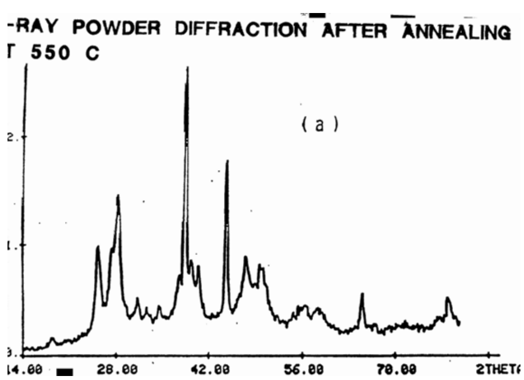


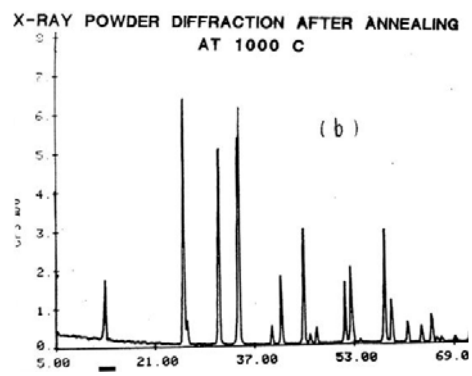
Fig. 10. XRD diffraction pattern of $Nd(OH)_2Cl$.

Chemical analysis of $Nd(OH)_2Cl$ samples

Sample	*Neodymium*	*Prasedymium*	*Chlorine*	*Oxygen*
1	65.9	0.5	16.3	17[a]
2	63.6	0.4	14.5	14
formula weight	67.5		16.6	14.9

[a]Less accurate due to double oxygen peaks.





DSC of $Nd(OH)_2Cl$

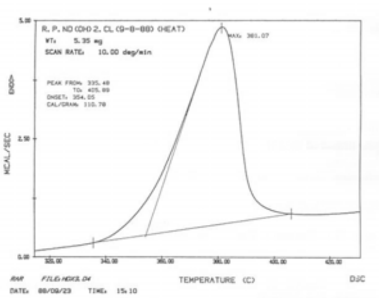
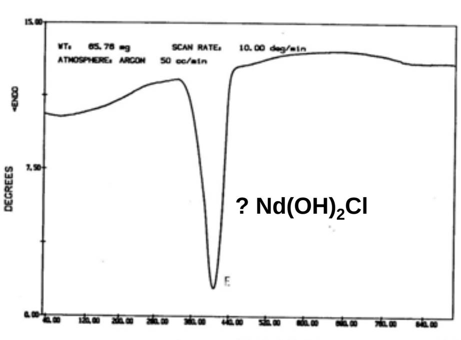


Fig. 14. DSC curve of $Nd(OH)_2Cl$.

DTA of Neodymium hydroxychloride



Analysis of neodymium trichloride dehydration

Differential thermal analysis (DTA) : detection of hydrates, hydroxychloride, and occluded water.

Wet chemical techniques **:** Elemental chemical analyses (for the Mg, Cl determination).

LECO oxygen determinator **:** Oxygen content determination.

Conclusions

- **One analytical technique cannot give answer to how much water (or its derivatives) is in the molten salt**
- **A combination of DTA, Wet chemistry (Mg, Cl and H) and LECO oxygen determination can give a very accurate picture at ppm levels.**

Summary

- **In 1970's and 1980's high current densities in copper electrorefining gets you fired!**
- **In 1990's you will be producing electrolytic copper powder for powder metallurgy!**
- **In 2000's you become an instant nanometallurgist!**

Future developments

- **Emphasize the university as a place to learn and think.**
- **Industry is not the playground to learn by making mistakes. The university is!**
- **Develop interdisciplinary teaching.**

Acknowledgements [personnel]

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