AN OVERVIEW OF EIGHT YEARS OF ACTIVITY DEVELOPING FRENCH NICKEL HYDROGEN TECHNOLOGY

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INTRODUCTION

- THE FRENCH AND EUROPEAN SPACE AGENCIES (CNES, ESA) HAVE BEEN CONTINUOUSLY CONTRIBUTING TO THE DEVELOPMENT OF SAFT NI H2 TECHNOLOGY SINCE 1985.

- AN IMPORTANT EFFORT HAS BEEN DEVOTED TO IMPROVING SCIENTIFIC KNOWLEDGE TO ENHANCING INDUSTRIAL EXPERIENCE AND TO PROMOTING SAFT AS AN OFFICIAL *"BACK UP SOURCE"* FOR THE EUROPEAN DOMESTIC TELECOMMUNICATIONS MARKET AS A BATTERY SUPPLIER.

- FUNDAMENTAL ASPECTS HAVE BEEN INVESTIGATED IN BOTH INDUSTRIAL AND UNIVERSITY LABS AS ESSENTIAL R & D SUPPORTS.

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OBJECTIVES

- WE INTEND TO EXPLAIN WHICH TECHNICAL AREAS, COMPONENTS AND PROCESSES HAVE BEEN COVERED BY OUR STUDIES

- WE INTEND TO SHOW THE RESULTS OF THIS WORK

- WE INTEND TO ESTABLISH THE STATUS WHICH HAS BEEN REACHED AND WHAT THE STANDARD SAFT IPV DESIGN'S MAIN FEATURES ARE

- WE INTEND TO PRESENT OUR PLANS FOR THE NEAR FUTURE

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HISTORICAL BACKGROUND
1984 - 1985 PERIOD

- ACTIVITIES AIMED AT BUILDING A 30-50 Ah IPV CELL DESIGN UNTIL 1984.

- LACK OF MECHANICAL CONCEPT MATURITY AND ELECTROCHEMICAL DISPERSION WERE OBSERVED.

- ENCOURAGING PRELIMINARY LIFE TEST RESULTS PERFORMED ON PROTOTYPES.

- DECISION TO START THE DEVELOPMENT ON A NEW IPV CELL DESIGN IN THE 30-50 Ah RANGE BY EARLY 1985

- **SPECIAL ATTENTION GIVEN TO MECHANICAL PART CONSTRAINTS** (MATERIAL, SHAPE, THICKNESS) **AND PROCESSES IN GENERAL :**
  . **MECHANICAL** (MACHINING, THERMAL TREATMENT, WELDING, CONTROL)
  . **ELECTROCHEMICAL** (IMPREGNATION, SORTING, FORMATION)

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1985 - 1992 DEVELOPMENT ACTIVITIES TECHNICAL REQUIREMENTS AND FEATURES

1985 - 1988 30-50 Ah "standard" cell VHS BL		1989 -1992 36-100 Ah "improved" cell VHS CM
. Energy density > 45 Wh/kg . GEO life expectancy : 10 years+	Goals	. Energy density 51-56 Wh/kg . GEO life expectancy : 12-15 years + EP cycles
. ∅ 3.2 Inches . 3 piece can . ceramic metal seals (rabbit-ear disposal) . 45° off set filling tube . tig weldings . 75 bars MOP . 2.5 mini safety factor . light Al alloy integral sleeve	Mechanical vessel	. ∅ 3.5 Inches . 2 symmetrical hydroformed parts . idem . polar filling tube . idem except filling tube/top dome (Yag) . Idem . 2 mini safety factor (EOL) . idem

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1985 - 1992 DEVELOPMENT ACTIVITIES
TECHNICAL FEATURES
ELECTROCHEMICAL / STACK DESIGN

1985-1988 30 - 50 Ah "standard" cell	1989-1992 36 - 100 Ah "improved"cell
- Mono stack/back to back	- Dual stack above 50 Ah
- Central tie rod/cont.lead assembly	- idem
- Rigid end plates/Belleville washer expansion system	- Light weight shaped end plates/star expansion system
	- Special molded central ring/stack fixture device
- IEC sintered positive electrode	- Thicker positive electrode (same hydroxyde and loading)
- platinized charcoal teflon bonded negative electrode	- Thinner negative electrode (improved catalyst and binder)
- Multi layered non woven polyamid felt separator	- idem
- Woven polyamid gas screen	- idem

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1985 - 1988 DEVELOPMENT ACTIVITIES
30 - 50 Ah range 3.2 inch cell validation results (VHS BL)

- **Medium capacity range IPV SAFT NiH2 cell development achieved by mid 1988**
- **Short term qualification testing realised successfully as follows :**
  . Accelerated fatigue testing on 3 structures : more than 150,000 cycles before leakage.

  . Burst testing on structures (under oil, He, H2 pressure) with/without sleeve : always more than 2.5 BOL security factor.

  . Safety testing on 8 cells (shock, short circuit, over discharge, overcharge) : good behaviour exhibited, cells still under life testing.

  . Thermal testing on 2 specially instrumented thermal prototypes : thermal cartography and correlation with predictive computer models.

  . Vibration testing on 6 cells : qualification loadings. No subsequent electrical or mechanical damage (3 cells life tested).

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1985 - 1992 ACTIVITIES
- 50 Ah CELL LIFE TESTING STATUS

<u>GEO applications</u>

- 9 cells (50 Ah) tested at SAFT facilities (3 vibrated)
- . 33 eclipse seasons completed under accelerated conditions (70 % DoD, 10° C max.)
- . More than 3 years of testing (Mid 1988-End 1991)
- . Average EOD voltage never below 1.16 V
- . 10 % capacity fading

- 9 cells (50 Ah) tested at AS facilities (3 abuse tested)
- . 17 eclipse seasons completed under accelerated conditions (70 % DoD, 10°C constant)
- . To be extended to at least 20 seasons
- . capacities remain stable EOD voltage > 1.10 V

<u>LEO applications</u>

- 4 50 cells (50 Ah) tested at ESA/ESTEC facilities (2 tappered, 2 non tappered) **at 35% DoD, 10 ° C**
- . 1 removed after 17,000 cycles, another after 31, 000 cycles
- . Former submitted to tear-down analysis

1985 - 1992 ACTIVITIES
30 - 50 Ah CELL LIFE TESTING STATUS (CONT.'D)

<u>LEO APPLICATIONS</u>

- **10 cells (50 Ah) tested at SAFT facilities** (40 % DoD - 15° C) **100 min. cycle, VT gestion**

  . more than 8,000 cycles performed

- **12 cells (50 Ah)** (4 with 26 % KOH) **tested at ESA/ESTEC facilities for Columbus project (90 min cycles, Ict or Pct charge and discharge ; 40 % DoD max and 10 ° C**

  . more than 6,000 cycles performed

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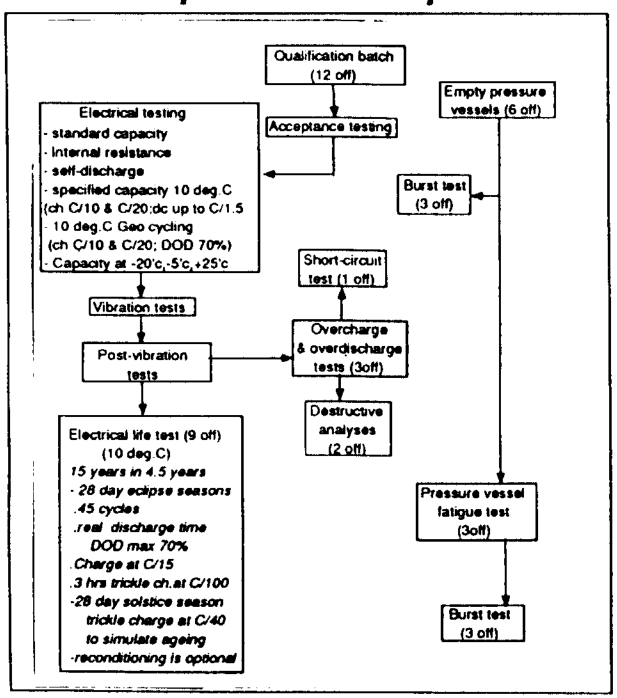
1989 - 1992 DEVELOPMENT ACTIVITIES
36 - 100 Ah 3.5 INCH CELL STATUS (VHS CM)

- High capacity range IPV SAFT Ni-H2 cell development achieved by March 1992.

- Short-term qualification sequence successfully completed

ESA qualification plan



VHS CM features

Capacity	(Ah)	40	50	60	70	80	100
Internal resistance	(mohm)	3.08	2.75	2.52	2.36	2.25	2.08
Mid-point voltage	(V)	1.26	1.25	1.24	1.24	1.23	1.21
Aver. capa. 10 deg.C	(Ah)	44	55	66	77	88	110
Mass	(g)	1097	1270	1467	1666	1865	2269
Height (with tube)	(mm)	169	182	208	234	259	310
Energy density	(Wh/Kg)	51	54	56	57	58	59
Specific energy (vessel only)	(Wh/L)	71	75	78	79	81	82

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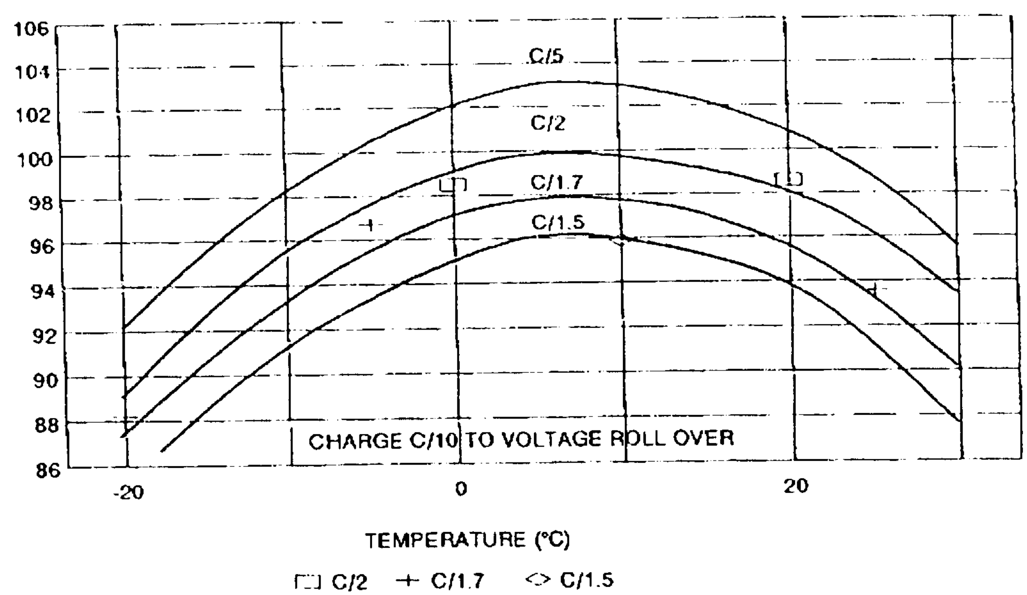
1989 - 1992 DEVELOPMENT ACTIVITIES
36 - 100 Ah O 3.5 INCH CELL STATUS (VHS CM)

VHS 90 CM QUALIFICATION RESULTS

BATCH OF 15 CELLS

CAPACITY TO 1 V VERSUS TEMPERATURE



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1989 - 1992 DEVELOPMENT ACTIVITIES
36 - 100 Ah VHS CM
VHS 90 CM QUALIFICATION RESULTS (CONT.'D)

- Pressure cycling tests performed on 4 structural vessels

. four time mission cycles under pure H_2

. burst pressure in the range 185 - 210 bars (SF > 2.5 EOL)

- Abuse testing on 5 cells

. C/10 24 hours overcharge : max. 94 bars stabilized pressure after 16 H

. C/1.7 1.2 hours overdischarge : min. 10 bars stabilized pressure

. short circuit on 1m : 450 A max. peak current, 113 Ah capacity down to 0V
1/2 H complete discharge step, 137° C max. Tre

. No direct effects observed, cells under life test

- Vibration testing on 12 cells

. quasi static sine 20 g

. random 28,7 g rms 200 - 400 Hz > 1 g2Hz peak

1989 - 1992 ACTIVITIES
90 Ah CELL LIFE TEST AT ESA FACILITIES

Goals

- To demonstrate at least 30 eclipse seasons in 4.5 years under semi accelerated conditions
- To evaluate the comparative effects of P ct versus I ct testing conditions
- To evaluate real thermal profile effects
- To establish pressure evolution and to validate strain gauge reliability mounting
- To simulate electric propulsion constraint

Materials and apparatus

- 20 VHS 90 CM cells split into 2 packs
- Peltier cold plate thermal regulation
- Integral sleeve/individual base plate socket/vertical mounting
- Thermal blanket styrenic foam
- Saturated dry nitrogen atmosphere with O2-controlled level
- 3 cells per battery with gage and pressure transducer

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1989 - 1992 ACTIVITIES
90 Ah CELL LIFE TEST (CONT.'D)

TEST CONDITIONS

Battery 1

Discharge regime	C/15, 60 A
Maximum DoD	80 %
Charge regime	C/15, 6 A
Recharge ratio	1/15
Floating regime	C/100, 0.9 A
Floating time	3 hours
Solstice regime	C/80, 1.12 A
Solstice time	28 days
Average temperature	10° C

Battery 2

Identical except

- constant power discharge
- possibility to replace solstice period by 21 days of 10 daily cycles at 40 % max. DoD for EP operation simulation

1989 - 1992 ACTIVITIES
90 Ah CELL LIFE TEST (CONT.'D)

Test operations

- Incoming inspection (visual inspection, open circuit voltage, insulation)
- Wake up testing
- Pre-check testings (standard capacity, voltage recovery, charge retention, internal resistance, capacity at mission regime, thermal validation)
- Storage
- Life testing
- Post-check testings (identical to pre-check)

Test chronology

- Batt 1 cells received by the end of may
- Sequences 1 to 4 in June and July
- TRR by the end of July
- Life test started in August
- 2 seasons achieved
- Batt 2 cells received by the end of October

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1985 - 1992 ACTIVITIES

GENERAL TECHNICAL AND MECHANICAL RESULTS

- **Good experience on part weldability (both tig and yag)**
  . validation program on parameter definition
  . leak + burst control
  . four fabrication lots (+ 80 cells)
- **Good knowledge of Inconel sensitivity to H_2 brittle effect**
  . ruptural disk method/parametrical studies wrt kinetic loading N_2/H_2 effect, KOH effect
  . comprehensive experimental program based on 200 coupon tests to establish
    * crack propagation law in an air and hydrogen atmosphere
    * hydrogen and KOH effects on propagation kinetic
    * crack shape ratio effect
    * frequency effects
- **Exhaustive mechanic fracture approach**
  . critical flaw size determination
- **NDI techniques evaluation and feasability studies**
  . RX dye penetrant, ultrasonic examination, eddy current probe, holographic testings

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1985 - 1992 ACTIVITIES

Mechanical results (cont.'d)

- Leak before burst demonstration (Analytical and experimental)
- Fatigue testing and demonstration
- Stack component characterisation versus compressibility and stiffness for dynamic constraint/design and life modelisation
- Study on internal ZrO2 plasma coatings

Thermal results

- Internal cell measurements and model correlations
- Extensive cell modelisation for prediction and design

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1985 - 1992 ACTIVITIES

ELECTROCHEMICAL RESULTS

- **Evaluation of performances with fibrous felt connector positive electrodes**
  . optimisation of active material loading, thickness, porosity and interconnection
  . boiler plate testing : more than 1200 accelerated cycles
- **Manufacturing and optimisation of a thin negative electrode**
  . new and very divided catalysts, light weight collectors and industrial hydrophobic layer
  . 30 % mass saving versus previous technology, 20 - 30 mV gain at C/2 discharge rate
- **Comprehensive studies on the relation between structural and electrochemical properties**
  . carbonate affinity Co3 effect, proton intercalation, network parameter evolution
  . effect of IEC temperature versus loading efficiency and β ex HN material
- **Patent related to "chimie douce" turbostatic α* new hydroxyde**
  . chemical stability in KOH, high electron efficiency, effect of particle size on cycling stability

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1985 - 1992 ACTIVITIES

ELECTROCHEMICAL RESULTS (CONT.'D)

- Comparative evaluation study on alternate separator material

. characterisation : thickness, porosity, traction resistance, compressibility, perforation resistance, electrolyte absorption and retention/compression effect, OH diffusion, capillary feature, gaseous permeability conductivity pattern/impregnation time, chemical resistance versus KOH and O_2 morphology, analytical composition for organic element

. materials : Zircar cloth, Asbestos felt, polypropylène, polysulfone, polyoléfine, standard non woven polyamid felt

. results : polyamid very competitive but Zircar and polyolefine are possible substitute

* zircar need to be treated because brittle for manipulation

* further investigations needed to assess long term behaviour

1985 - 1992 ACTIVITIES

TEAR DOWN ANALYSIS RESULTS

GOALS

- Establish a BOL reference state

- Explain and quantify component degradation
- Use a technical feedback source on design parameters

OPERATIONS

- Leak test + phenolphthalein test
- Strength test on parts
- Welding controls
- Dimensional controls on stack and mechanical components
- KOH + K_2CO_3 concentration and repartition
- Electrical tab controls
- Insulation and resistance controls
- Positive swelling measurement
- X- Ray pattern for active materials at positives
- Porosity, BET and I/V curves on negatives
- Compression curves on expansion system

RESULTS

- one GEO cell failed after 27 seasons
- lack of vessel insulation
  . galvanic coupling
  . O_2 evolution and internal short circuit

- positive swelling 2.1 % (0-10 %)
- negative compression 5.4 %
- K_2CO_3 in -
- KOH amount in + ↗ in sep ↘

- support attack level ↗
- Δ porosity coupled with Δe at positive
- new micro porosity
- larger cristallite size at +
- separator not altered
- confirmation on LEO cell after 1600 cycles

FUTURES ACTIVITIES

GEO

- Cycling test on 20 90 Ah cells till 1996 - 1997

LEO

- Cycling test on 10 50 Ah cells till 1995
- Qualifiction on 40 - 70 Ah battery by mid 1993
- Specific LEO design development to be terminated by end 1993
- Selection, testing for LEO/new separator materials (zirfon, PS0 asbestos cloth)
- Definition and study/new foam based positive electrode to reach 65-70 Wh/kg for GEO
- Understanding study on optimisation / new hydroxydes materials-new supports new binding technologies
- Testing on hydrides cells + fundamental studies on new AB materials for improved performances

1985 - 1992 CNES/ESA NiH2 DEVELOPMENT ACTIVITIES

SUMMARY/CONCLUSIONS

- Since 1985 CNES has been leader in developping basic technologies improving scientific knowledge and entrancing industrial capability with SAFT but also others partners.
- Helpfull ESA participation permit to achieve successfully a generic qualification status on a new broad range (36-100 Ah) GEO cell definition.
- SAFT is providing today a large experience, a serious background and an efficient data base to design new materials and components to fit extensive needs.
- Mechanical and thermal software tools based on experimental correlations to be performed in a general battery qualification program will deliver basis for a full compliant range of batterie for current applications in the next fine years.
- Specific works are on going to develop a LEO design cell while a light weight positive electrode is define to replace traditionnal sintered electrode to achieve mass saving goals for high power future GEO applications

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