EXPERIENCE WITH A NEW FILLING PROCESS FOR VRLA BATTERIES IN GEL TECHNOLOGY

LABAT 2017

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Overview

- Description of „Gel circulation „process
- First filling of OPzV
  - Process and cell performance
- Filling of PzV and VRLA blocks
- Quality and performance
- Economy of the process
LEAD ACID BATTERIES

FLOODED

VALVE REGULATED (VRLA)

Cells
(2 volt OPzV/PzV)

Blocks
(6/12 Volt)

GEL

AGM
EXPERIENCE WITH A NEW FILLING PROCESS FOR VRLA BATTERIES IN GEL TECHNOLOGY

VRLA GEL

COLLOIDAL
- easier to handle
- easy mixing
- Lower cost of equipment
- Vacuum filling not needed

FUMED
1. direct GEL filling
   - formed plates
   - unformed plates
2. Two shot

New: GEL circulation

works for GEL batteries in stand-by operation

Recommended for GEL batteries in cycling operation
# EXPERIENCE WITH A NEW FILLING PROCESS FOR VRLA BATTERIES IN GEL TECHNOLOGY

<table>
<thead>
<tr>
<th>METHOD</th>
<th>PROCESS</th>
<th>PRODUCT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. DIRECT GEL FILLING</strong></td>
<td>costly process environment concern high energy consumption</td>
<td>best quality</td>
</tr>
<tr>
<td>- formed plates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- unformed plates</td>
<td>low investment in equipment long formation process high energy input no H$_3$PO$_4$ possible</td>
<td>reasonable quality; On average lower capacity</td>
</tr>
<tr>
<td><strong>2. TWO SHOT</strong></td>
<td>costly equipment many handling steps</td>
<td>good quality</td>
</tr>
<tr>
<td><strong>New: GEL CIRCULATION</strong></td>
<td>low cost equipment fast and clean process</td>
<td>good to best quality</td>
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</tbody>
</table>
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Step 1
Formation
Acid circulation

Step 2
GEL filling
circulation

Step 3
Charging
equalization

Patent number: WO 2016/0008503 A1
Step 1

Formation

Filling - soaking

Formation

Acid increase - adjustment

Discharge- cap.test

Quality control
- Checking of capacity of flooded cell
- Identification of any weak cells
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Step 2

GEL - circulation

GEL mixing (fumed)

GEL circulation

Step 3

Charging equalization

charging

Quality check
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PRINCIPLE OF FILLING PROCESS

- Acid tank
- Gel mixing tank
- OPzV cells
- Pump
- Dead end plug
- Gel transport tubes
- Filling plugs
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VIEW OF THE MIXING & CIRCULATION MACHINES

Gel filling unit
Buffer tank
Mixing tank
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VIEW OF THE CIRCULATION EQUIPMENT
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32 cells of OPzV 600

- OPzV cell
- Sulphuric acid
- Increase of SiO₂

- GEL-mixing tank
- Lowering SiO₂ content

% SiO₂ tank vs. % SiO₂ cells

- % SiO₂ tank
- % SiO₂ cells
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Calculation principle
Acid volume in mixing tank: 350 kg
Filling volume OPzV 6/600: 10 kg Number of cells: 30
Target SiO₂ in OPzV: 5,8%

INITIAL / FIRST FILLING PROCESS

30 x 10 = 300 kg total Acid volume cells
Total volume acid cells plus GEL tank: 350 + 300 = 650 kg
5,8 % SiO₂ in 650 kg requires 40 kg SiO₂ (total weight: 690 kg)

FOLLOWING FILLING PROCESS

GEL volume in mixing tank: 350 kg SiO₂ concentration: 5,8 %
Same cell type and quantity: 300 kg of acid
Same 5,8% SiO₂ in cells requires 18,3 kg SiO₂
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OPZV - data

high pressure safety valve

Manufacturing/filling process

PAM
Internal cell pressure of a OPzV cell during cycle life test

- Little gassing only
- No neg. pressure in the cell

Particular critical for AGM products

Due to gas loss negative pressure in the cell

>50 % of charging time above 80 mbar

Gassing Waterloss

VALVE 80 mbar

VALVE 200 mbar

mbar

OPZV - data
Cell capacity of 6 OPzV 600 after first charge
C10 rated: 733 Ah

Cap. Ah

100 % line
C10 discharge curves of 6 OPzV 600 after first charge
C 10 rated: 733 Ah
### OPZV - data

#### C10 _ 5OPzV 350 (420Ah)

<table>
<thead>
<tr>
<th>cell</th>
<th>Description</th>
<th>C10 (Ah) &amp; % at 20° C</th>
<th>C10 (Ah) &amp; % at 25° C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ah</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>1 # without phosphoric acid vertical</td>
<td>450,0</td>
<td>107,1</td>
</tr>
<tr>
<td>2</td>
<td>2 # without phosphoric acid vertical</td>
<td>462,2</td>
<td>110,0</td>
</tr>
<tr>
<td>3</td>
<td>3 # Phosphoric acid vertical</td>
<td>424,3</td>
<td>101,0</td>
</tr>
<tr>
<td>4</td>
<td>4 # Phosphoric acid vertical</td>
<td>425,0</td>
<td>101,2</td>
</tr>
<tr>
<td>5</td>
<td>5 # Phosphoric acid Horizontal</td>
<td>399,3</td>
<td>95,1</td>
</tr>
<tr>
<td>6</td>
<td>6 # Phosphoric acid Horizontal</td>
<td>392,6</td>
<td>93,5</td>
</tr>
</tbody>
</table>
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PZV - data

3 /213 PzV-BS cells voltage during 1st discharge

3 13 mV

00:00 02:24 04:48 07:12 09:36 12:00

09:57 10:04 10:12 10:19 10:26 10:33

100,0 120,0 140,0 160,0 180,0 200,0 220,0 240,0 260,0 280,0 300,0

1 2 3 4 5 6

100% line
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PZV - data

3 /300 PzV cells voltage during 1st discharge

[Graph showing voltage decrease over time with a notable drop of 17 mV]
3PzV 300 cycle test (6 cells) end voltage 1.7vpc; 30°C

- Gel circulation
- Two shot; acid drainage

1 cell removed (filling problems)
After acid drainage

Depending on time from acid drainage to Gel filling = increasing heat on neg. plate

- oxidation
- surface drying
- rapid gelification

FILLING FAILURES

GEL- circulation

Plates always covered with liquids
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- less equipment (acid drainage, filling machine)
- Less waste material (no acid recycling)

Cost saving about 3 to 11 % per cell/block
- Better quality

Formation and 2% discharge

TWO SHOT GEL FILLING PROCESS
- Acid drainage
  - Machine/equipment
  - Vacuum filling machine
- Gel vacuum filling
- Final charging

GEL CIRCULATION FILLING PROCESS
- Gel circulation
- Final charging

Machine/equipment
- Acid treatment
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SUMMARY:

- Less investment, no acid drainage, no vacuum filling

- One filling unit for all types of products (cells/blocks)

- Faster process in production (time saving)

- No waste material (drained acid)

- Almost no risk of filling problems

- Good product quality
  - Neg. plates not exposed to air
  - Perfect distribution of GEL
  - High consistency of cell performance
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THANK YOU

QUESTIONS ? SEE US AT THE ABERTAX BOOTH
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**OPzV – GEL Technology**

**Improvements in design**

**Fumed or colloidal Silica?**

**Fumed silica**

\[ \text{SiCl}_4 + 2\text{H}_2 + \text{O}_2 \rightarrow \text{SiO}_2 + 4\text{HCl} \]

Amorphous partials

2 – 15 nm

**Colloidal silica**

\[ 2\text{H}_4 \text{SiO}_4 \rightarrow \text{H}_6 \text{Si}_2\text{O}_7 + \text{H}_2\text{O} \]

\[ 2\text{H}_6 \text{Si}_2\text{O}_7 \rightarrow \text{H}_{10}\text{Si}_4\text{O}_{13} + \text{H}_2\text{O} \]

**Tixotrophic system**

Fumed silica

Colloidal silica

Amorphous partials

2 – 15 nm

**Fumed or colloidal Silica?**

**Fumed silica**

Amorphous partials

2 – 15 nm

**Colloidal silica**

**Tixotrophic system**

Fumed or colloidal Silica?
The Cycle Life Curves of IB44-6 for Experimental Batteries

Remark:
1. Discharge: Constant current 9A, Final voltage 5.10V;
2. Recharge: Max current 9A, Constant voltage 7.05V charge for 14 hours;
3. Ambient temperature: 35±5 °C;
4. According to: IEC 60254-1 2005 5.5.3.2

Impact of „Gel System“ on battery performance

OPzV – GEL Technology
High quality (pressure) valve

What closing pressure?
What tolerance of opening and closing pressure?
High quality (pressure) valve

OPzV – GEL Technology

Patent Protection on all Products
Waterloss is the main failure mode for ”good” VRLA batteries - for all stand-by and particular motive power products -

Before test

After 100 cycles

After 200 cycles

30 mbar valves

170 mbar valves

6% loss of electrolyte

13% loss of electrolyte

IBRX - 2012
High quality (pressure) valve

Internal cell pressure of a OPzV cell during cycle life test – 80 mbar valve

30 hours charge and discharge
12- 14 hours recharge time; 65 % of this time > 80 mbar

OPEN VALVES ! - GASSING !

Opening pressure of the valve 80 mbar

Negative pressure
Internal cell pressure of a OPzV cell during cycle life test – 200 mbar valve
Internal cell pressure of a OPzV cell during cycle life test – 80 mbar valve

What happens above 80 mbar??

Opening pressure of the valve 80 mbar

Negative pressure

IBRX -2012