The “DCA Memory” Effect

Section 2B0 – Global Collaboration to Understand the Effect

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The Definition of "DCA Memory"

- **Dynamic Charge Acceptance (DCA)**
  - A variable describing how effectively a battery recovers charge under test protocols mimicking real-world operation
  - Provides a benchmark for automotive manufacturers choosing a battery system for micro-hybrid operation
  - Higher is better, indicating improved charge absorption and more efficient use of alternator current

- **During development of the DCA measurement method, and in other labs since, the variable was observed to change as a function of previous CHR or DCH history giving rise to the concept of "DCA Memory"**
  - The DCA current was higher if measured after a DCH process (ex. I_D in EN 50342-6:2015)
  - The DCA current was lower if measured after a CHR process (ex. I_C in EN 50342-6:2015)
  - The DCA current would lower over start/stop operation but stabilize, maybe recover, in duty (ex. "Run-in" DCA)

Three Potential Mechanisms

- **Lead-acid battery experts have suggested 3 theories to explain "DCA memory", but there may be more:**

1. ***Local Electrolyte Effect***
   - Localized perturbations in SG following DCH (low SG) or CHR (high SG) provide a basis for hi/lo conductivity/current
   - These local differences in SG are the physical embodiment of "DCA Memory"

2. ***Lead Sulfate Ripening***
   - During DCH/CHR cycles, a subset of lead sulfate crystals reach a critical surface tension/energy which stabilizes them against dissolution, leads to gradually decreasing supply of Pb^{2+}, and decreases charge current, particularly in Run-In
   - These crystals become the physical embodiment of "DCA Memory"

3. ***A Perturbation of Pb^{2+} Diffusion Kinetics***
   - Pb^{2+} availability defines charge rates but the polymer-dynamics-defined release of Pb^{2+} from battery organics at high acid/salt (high SoC, or CHR-1st protocols) or low acid/salt (low SoC, or DCH-1st protocols) concentrations could explain the enhanced availability of Pb^{2+} following DCH
   - The interaction of organic, Pb^{2+}, and local environment is the physical embodiment of "DCA Memory"

A Global Initiative To Explore the Memory Effect

The DCA Memory Effect: An investigation of the respective influence of battery physical characteristics.

Contributing Authors:
E. Karden, M. Raiford, S. Christie, P. Everill, J. Settelein

1. Purpose

Dynamic charge acceptance (DCA) of a lead-acid battery is dependent on the way the battery attained a given state of charge: by recent discharging, recent charging, or after extended microcycling. DCA may differ by factors of 4 to 10 for identical cells at the same temperature and same SOC, even after long (e.g., 20 h) rest. This has been described as **DCA memory effect**.

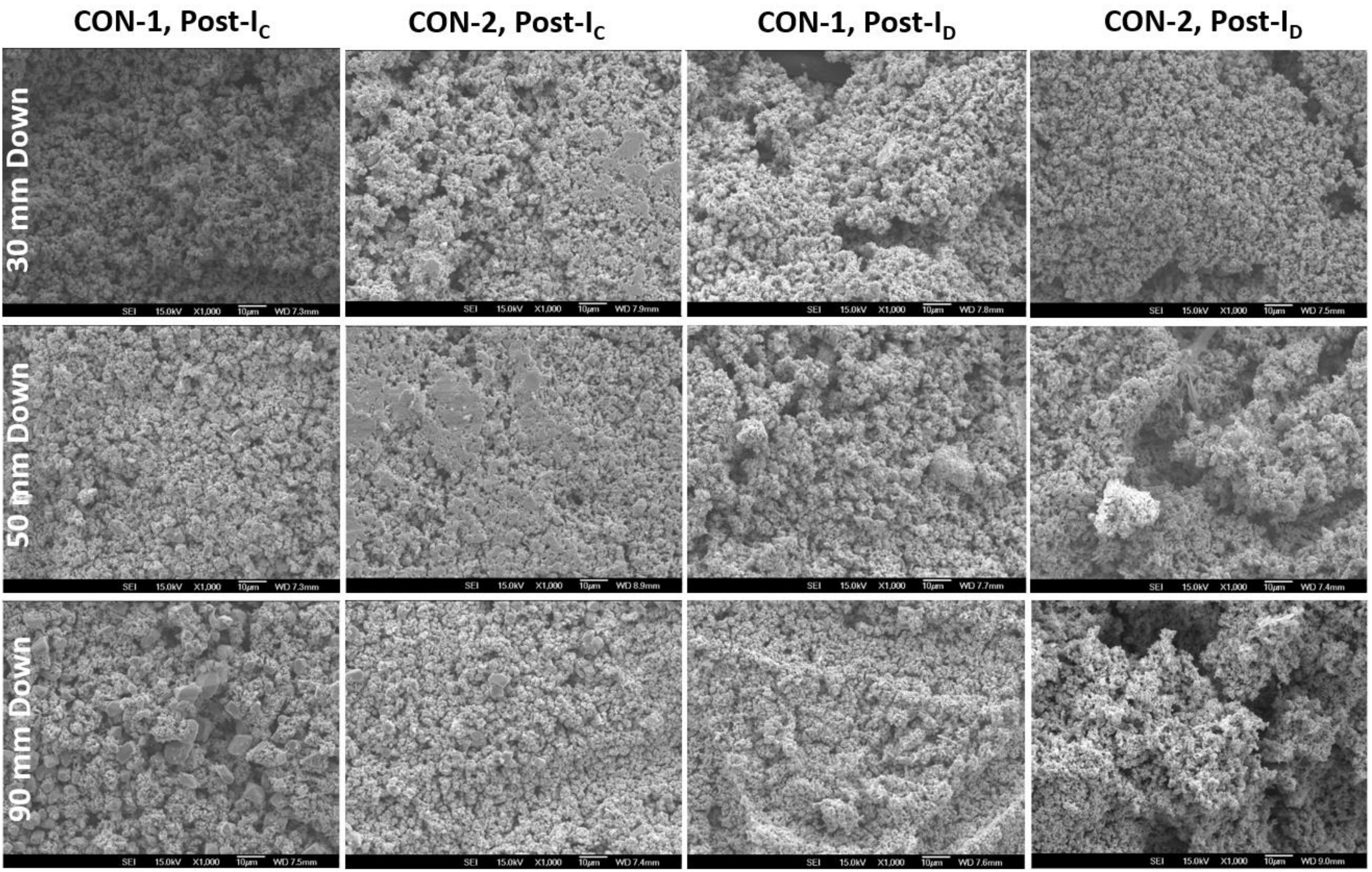
Half-cell measurements indicate that the DCA memory effect is caused by differences which occur at, or within, the negative electrode. Observation of acid densities over macroscopic distances within time periods like 20 h indicate electrolyte (sulfate) concentration effects are unlikely to play a significant role. It is therefore expected the memory effect is an expression of differences in the physical microstructure of the negative active material (NAM), or an as-yet-to-be-demonstrated surface-interactive process. Most literature would link these phenomena to solubility (and sometimes diffusion) of Pb^{2+}. Ostwald ripening (in rough words: recrystallization, healing, and merging of initially formed small crystallites) is a plausible mechanism that could result in such significant reduction of $PbSO_4$ solubility. Yet there is no published evidence for NAM microstructure differences related to DCA variation.

This document proposes a joint testing and analytical effort with two purposes:

1) *Reality check for CBI Best Practices:* Over recent years, CBI has systematically collected and made available best practices for test-cell design and manufacture, DCA testing, and material sample preparation. It is time to apply them in several labs for a manageable test program (only a few days of electrical testing per cell) and a clearly defined hypothesis for material investigation. As a result, Best Practices will be revised and clarified wherever issues may occur.
2) *Find the microstructural nature of DCA variation:* The DCA memory effect provides an excellent opportunity to investigate the difference between NAM of identical chemical composition (e.g., average $PbSO_4$ content, additives) but vastly different DCA performance following charge or discharge during the 2 days before DCA measurement. Starting the investigation with standard production (baseline) NAM will avoid confidentiality problems. It may be hypothesized that "high-DCA" additives would create a similar charge-willing microstructure as is achieved in "freshly discharged" NAM, but permanently. It should be straightforward to test this and similar hypothesis once the basic procedure has been established.

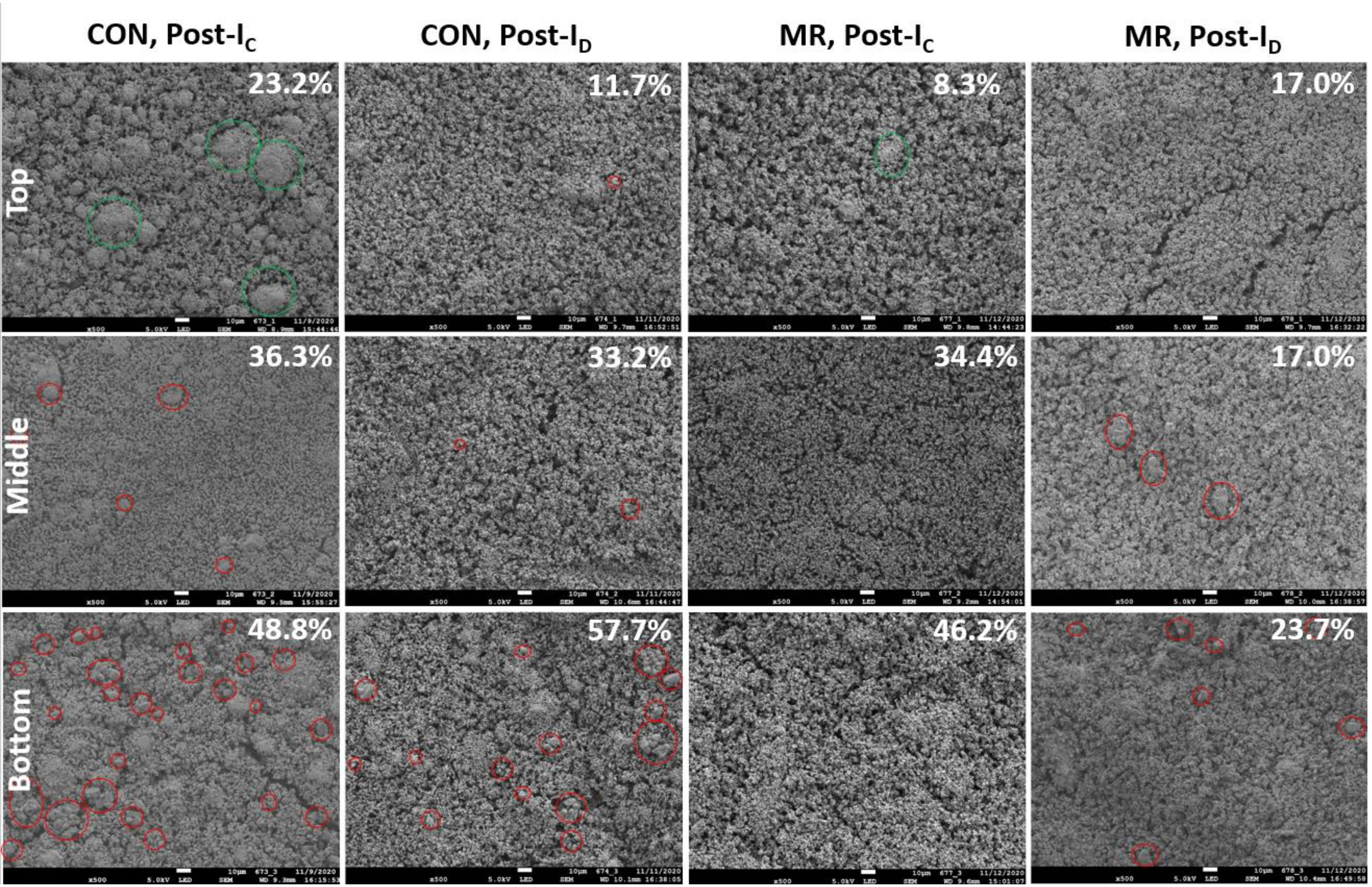
- **Since ALBA 2019 (Bruges), five global labs have been working to understand the mechanism behind this observation**
  - ArcActive, LTD
  - Black Diamond Structures, LLC
  - Clarios
  - East Penn Manufacturing
  - Fraunhofer, ISC
- **A unified method was discussed, defined, and rolled-out to all groups participating to enable paralleled observations to be made**
- **Results were acquired between 2020-2021**

ArcActive, LTD



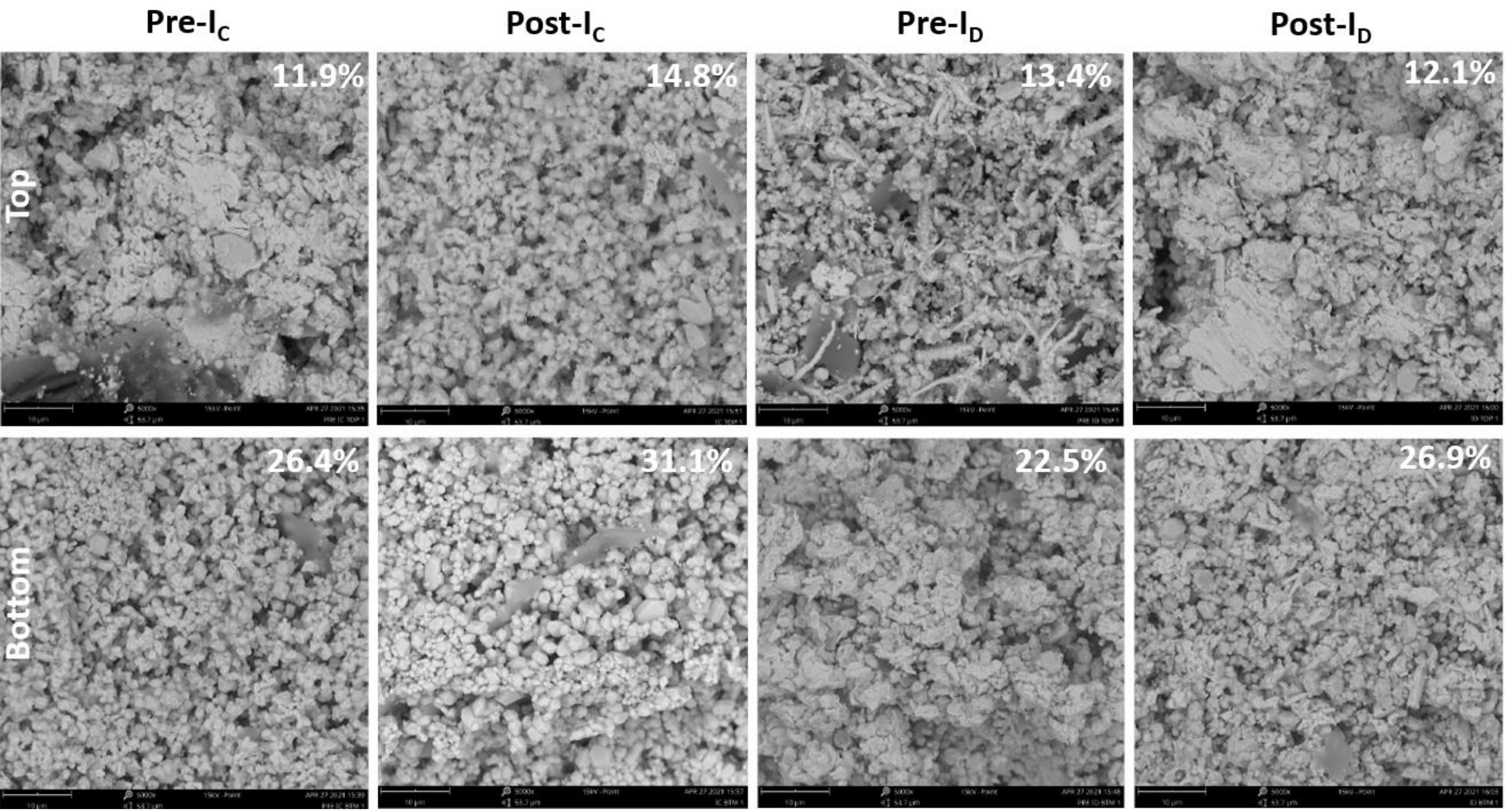
- I_D/I_C ~ 3-4 (I_C @80%, I_D @90%)
- Reference electrode indicated negative electrode limited
- Strong active material stratification, especially post-I_C
  - $PbSO_4$ is larger, more obvious lower on the plate
- 1000X magnification

Black Diamond Structures, LLC



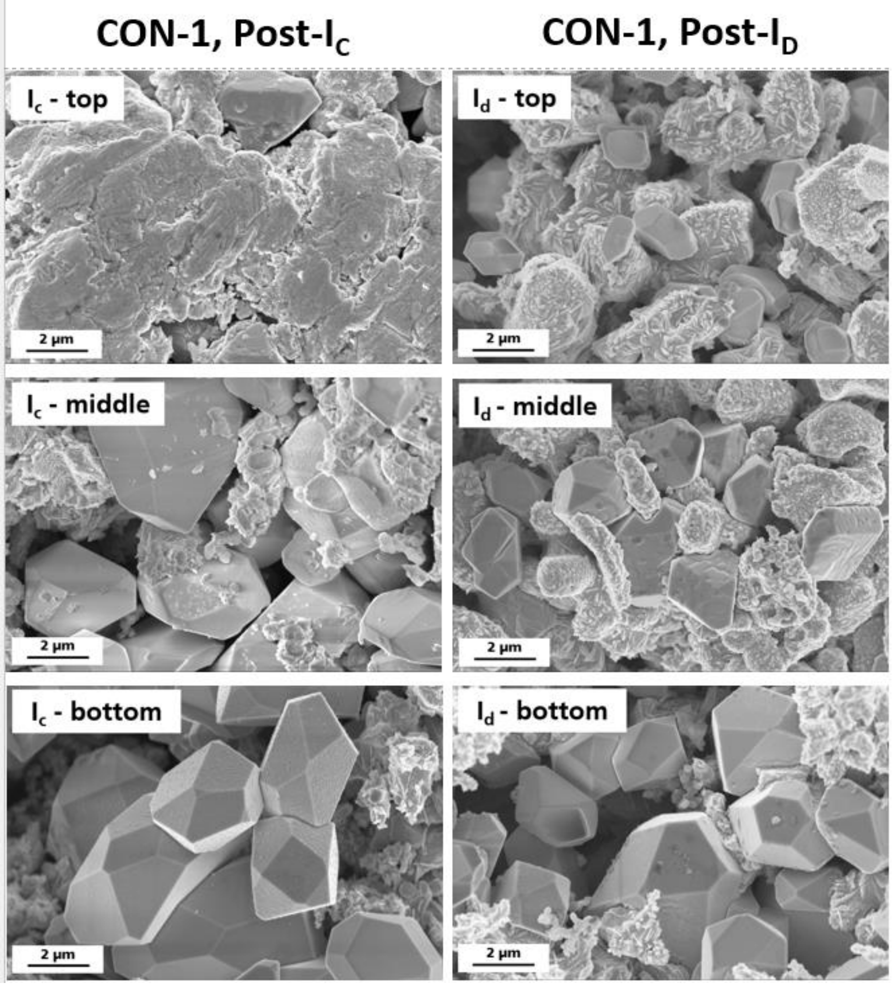
- I_D/I_C ~ 5.5
- **Strong AM stratification**
  - $PbSO_4$ in red circles
  - crystal clusters post-I_C (green circles),
- **I_D charging focused near tab?**
- **MOLECULAR REBAR® improved AM consistency, especially after I_D**
- **500X magnification**

East Penn Manufacturing



- **Strong AM stratification in I_C and I_D**
  - I_C is stratified the most
- **Images corroborate XRD**
  - $PbSO_4$ indicated in white numbers
- **Mercury Intrusion Porosimetry open to interpretation**

Fraunhofer ISC



- I_C showed larger $PbSO_4$ than I_D
- The bottom of the plate had larger $PbSO_4$ crystals than the top
- Bottom/top difference more pronounced than I_C/I_D

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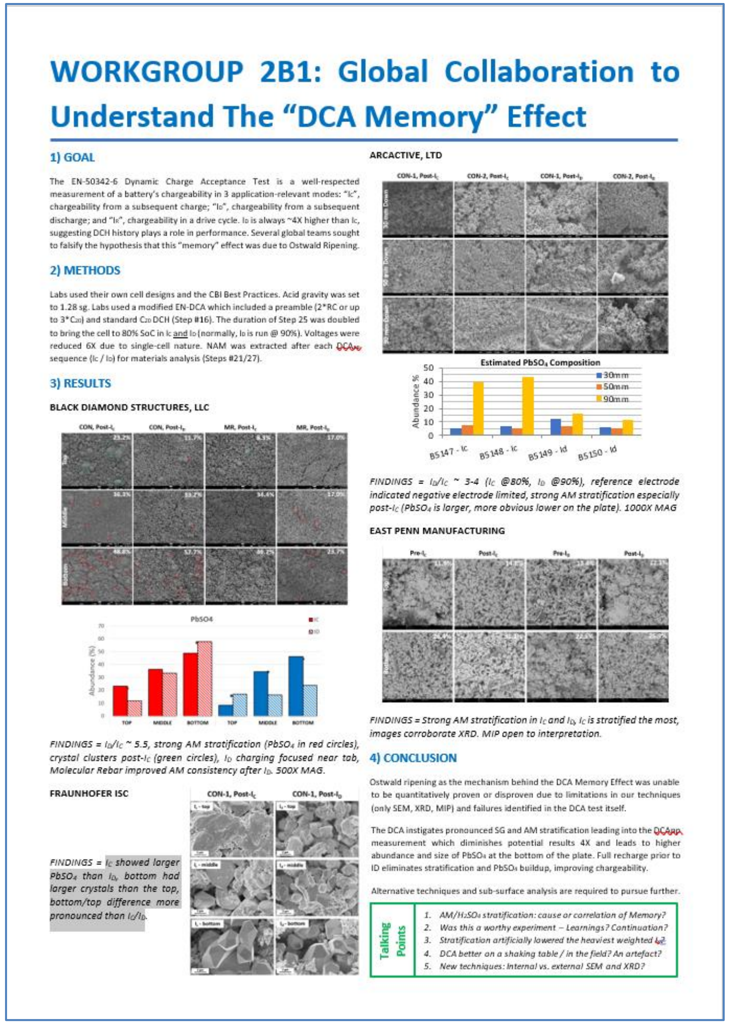
Discussion Points for the Poster Session

- **Active Material / Electrolyte stratification is identified in all labs**
  - Is this the cause of the DCA Memory, or a correlation?
  - If this stratification could be removed, would DCA Memory disappear?

- **Was this a worthy experiment?**
  - What did we learn?
  - What are our next steps?
  - Are there new techniques which could be used to explore the concept?

- **DCA Test Interpretation – is the test biased for the least relevant I_X?**
  - I_C has the worst stratification due to the preamble, and I_D is partially recovered thanks to the full charge following DCApp Part 1
  - Is this application relevant? Are we artificially lowering DCA magnitude?
  - DCA better on a shaking table / in the field?



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