

# Low Regeneration Temperature Sorbents for Direct Air Capture of CO<sub>2</sub>

## primary project goal

Susteon Inc., in partnership with the University of Wyoming (UWy), is working to develop solid sorbent materials that have much higher working carbon dioxide (CO<sub>2</sub>) capacity and can be regenerated at lower temperatures than current state-of-the-art materials. Structured sorbent beds can be constructed using these sorbents for low pressure drop operation to achieve reduced costs for direct air capture (DAC) of CO<sub>2</sub>. The project aims to develop amine-doped solid sorbents catalyzed by a novel ionic liquid (IL) that have the potential to increase the CO<sub>2</sub> adsorption and desorption rate by several orders of magnitude as compared with non-catalyzed sorbents.

## technical goals

- Develop amine-doped solid sorbents catalyzed by an IL that have the potential to increase the CO<sub>2</sub> desorption rate by several orders of magnitude at desorption temperatures of approximately 80°C.
- Evaluate the catalyzed amine-based sorbents to determine CO<sub>2</sub> desorption and adsorption kinetics.
- Based on the experimental results, develop a conceptual process design for the sorbents applied in a DAC system and conduct a preliminary cost analysis to assess the potential of the novel sorbent to reduce the cost of DAC.

## technical content

Sorbents for DAC application must have several characteristics: (i) high selectivity for CO<sub>2</sub> adsorption over the other components present in the air (such as nitrogen [N<sub>2</sub>] and oxygen [O<sub>2</sub>]), (ii) high CO<sub>2</sub> working (adsorption) capacity, (iii) mild conditions for regeneration (usually induced by pressure or temperature swings), (iv) high stability and resistance against impurities and moisture, and (v) fast CO<sub>2</sub> adsorption and desorption kinetics. Amine-doped solid sorbents have been proven effective for DAC and can be regenerated by heat or by a combination of heat and steam. Lowering the regeneration temperature, and hence opening a way to use waste heat for sorbent regeneration, can significantly lower the cost of DAC. The IL catalysts can be easily added to amine-doped solid sorbents because the IL is not volatile and can be easily mixed with possible amine molecules such as polyethyleneimine (PEI), polypropyleneimine (PPI), etc. Furthermore, their catalytic effect has been studied extensively at UWy and proven effective when added in parts per million (ppm) concentrations in a monoethanolamine (MEA) solution. The IL has also been added to commercial amine-doped silica sorbents and tests have shown that the IL is effective in catalyzing solid sorbents for DAC applications with increased CO<sub>2</sub> working capacity, as well as adsorption and desorption kinetics. This combination of industrially utilized amine-based sorbents with a proven catalyst to form a new class of materials for DAC provides a technically viable pathway for reducing the cost of DAC to less than \$100/tonne of CO<sub>2</sub>.

### program area:

Carbon Dioxide Removal

### ending scale:

Laboratory Scale

### application:

Direct Air Capture

### key technology:

Sorbents

### project focus:

Amine-Doped Sorbent Catalyzed by Ionic Liquid for Direct Air Capture of CO<sub>2</sub>

### participant:

Susteon Inc.

### project number:

FE0031965

### predecessor projects:

N/A

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### partners:

University of Wyoming

### start date:

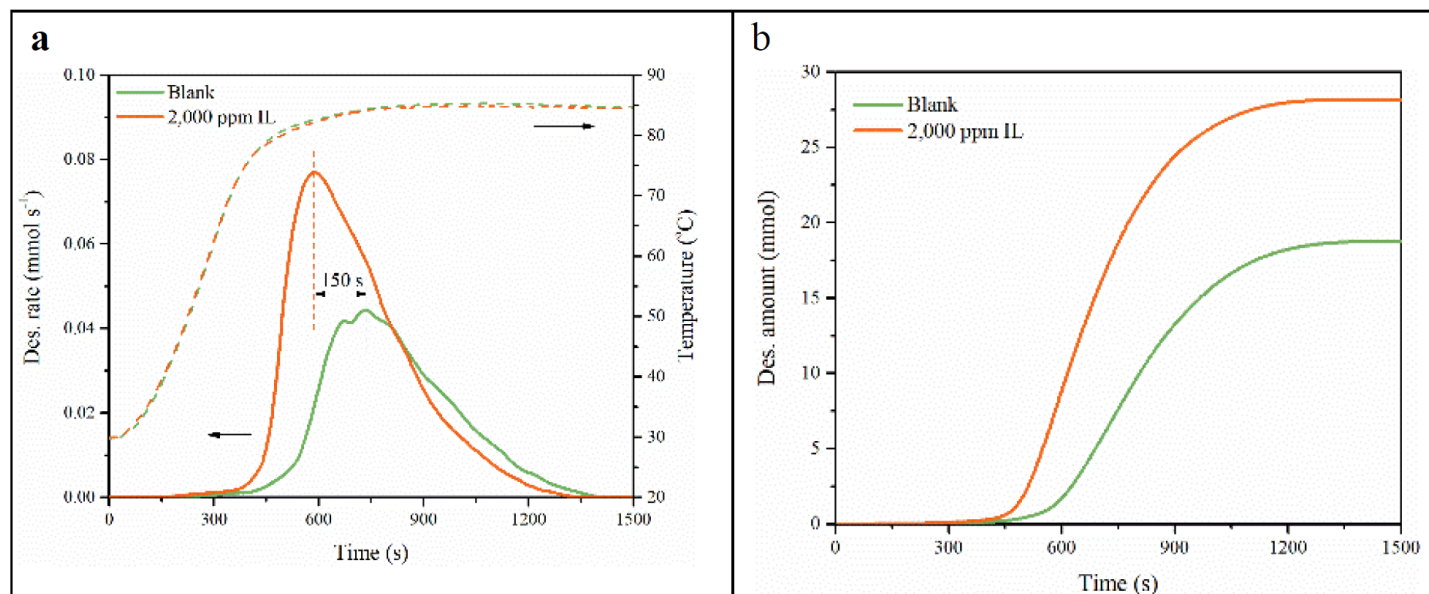
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### percent complete:

82%

ILs, consisting of organic cations and organic or inorganic anions, are environmentally friendly due to their various desired characteristics, including high chemical/thermal stability, tunable physicochemical characters (acid/base sites), low corrosiveness, and low heat capacity, which is highly desirable for CO<sub>2</sub> capture systems. This project is aimed at utilizing the catalytic activity of a novel IL for DAC application by improving CO<sub>2</sub> adsorption and desorption kinetics. A new bifunctional IL has been discovered with the functionality for high catalytic activity in CO<sub>2</sub> capture solvents and sorbents due to the presence of Brønsted acid sites. This IL has been successfully used for significant acceleration of chemical reactions between amines and CO<sub>2</sub>. It has also been utilized in modifying other catalysts for improving their catalytic performance. Nevertheless, it has never been used for enhancing the performance of solid CO<sub>2</sub> capture agents prior to this work, but has shown promising results with liquid amines (discussed later in this technology sheet). This project is focused on integrating this IL catalyst into amine-doped solid sorbents to develop a new generation of CO<sub>2</sub> capture sorbents with significantly higher adsorption and desorption rates and lower desorption temperatures (~80°C).

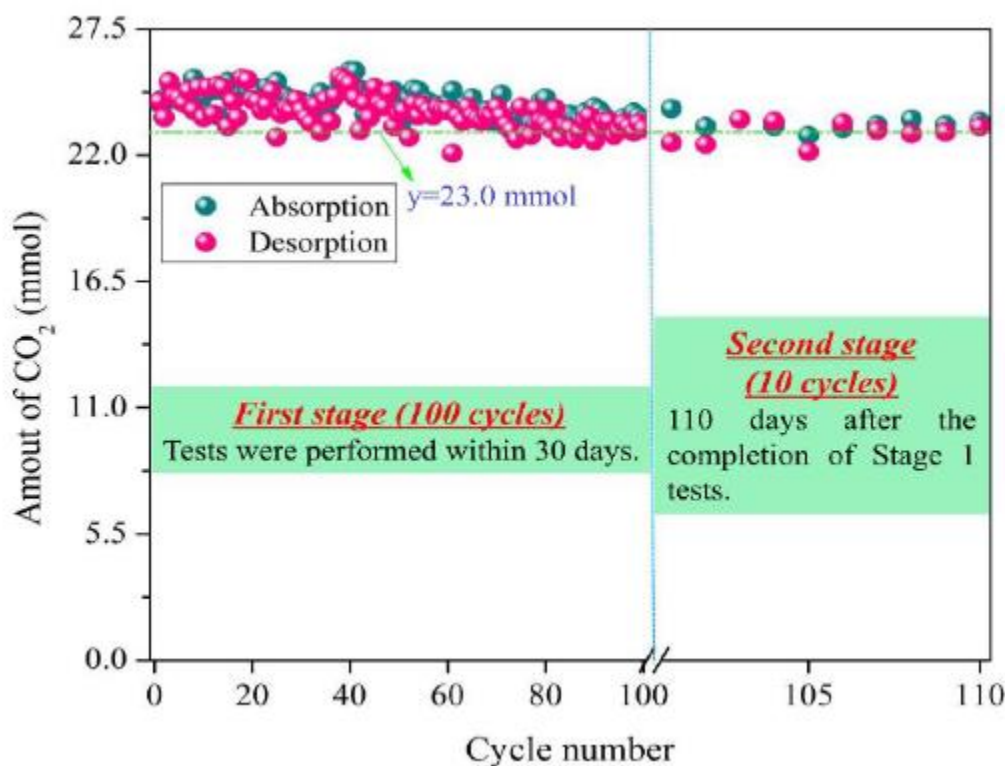
Previous tests were carried out to measure CO<sub>2</sub> absorption and desorption performance with 20 wt% MEA solution catalyzed by the IL catalyst. The absorption process was carried out with 100 grams of absorbent solution with a gas flow rate of 500 mL/min. The gas was composed of 80 vol% N<sub>2</sub>, 10 vol% CO<sub>2</sub>, and 10 vol% O<sub>2</sub>, which is similar to a typical flue gas composition from a coal-fired power plant, except for the higher O<sub>2</sub> content. The absorption process was carried out until 13 minutes. The optimal IL dosage was found to be about 2,000 parts per million weight (ppmw) for this case. As shown in Figure 1, the IL catalyzed both CO<sub>2</sub> absorption and desorption processes (green is without the IL addition) and (orange is with IL addition).



**Figure 1: Catalytic effect of IL on CO<sub>2</sub> absorption and desorption. (a) Effect of CO<sub>2</sub> desorption rate with and without catalyst; (b) effect of catalyst on the quantities of desorbed CO<sub>2</sub>.**

The desorption rate improvement obtained with the IL catalyst can reach as high as 175% (Figure 1a, 0.07 mmol s<sup>-1</sup> versus 0.04 mmol s<sup>-1</sup>), and the time required to reach the maximum desorption rate with the IL catalyst is shortened by 150 seconds (Figure 1a), in comparison with that for un-catalyzed CO<sub>2</sub> desorption. As shown in Figure 1b, the total amount of CO<sub>2</sub> desorbed increased significantly from 18.7 mmol to 28.2 mmol, an improvement of 51% when the IL catalyst was used as an additive to the MEA solvent. These experimental results clearly show that the IL is quite effective for catalyzing the CO<sub>2</sub> absorption and desorption processes.

The long-term stability of the IL catalyst for CO<sub>2</sub> absorption-desorption was studied with 110 cyclic tests in a time period of more than five months. The results of the long-term cyclic testing are shown in Figure 2, which shows that there are no evident changes in both the quantities of absorbed and desorbed CO<sub>2</sub> within the 100 cycles in first-stage testing. The 100 cycles of CO<sub>2</sub> absorption-desorption testing were carried out in a 30-day period. The average working CO<sub>2</sub> capture capacity within the 100 cyclic tests conducted in the 30-day period was 23.2 mmol per 100 mL of solvent, which was very close to the 24.3 mmol per 100 mL of solvent obtained in the first run. The slight decrease was due to the accumulative MEA losses, resulting from the difficulty in condensing and recycling the regenerated MEA in each CO<sub>2</sub> desorption step from the carrier gas stream. It is to be noted that loss of active amine in the solvent will also occur in large-scale industrial applications due to emissions and degradation.



**Figure 2: Demonstration of stability of MEA/(EMmim<sup>+</sup>)(NTF<sub>2</sub><sup>-</sup>) CO<sub>2</sub> capture system in cyclic CO<sub>2</sub> absorption-desorption tests for more than five months.**

To further confirm the outstanding stability of the MEA/IL-based CO<sub>2</sub> capture solvent, 10 more cyclic or Stage 2 tests were performed after 110 days after completion of the first 100 cycles or Stage 1 tests by using the same MEA/IL solvent used in Stage 1 tests. For Stage 2, each of the cyclic test results are shown in Figure 2, where it can be seen that the average working CO<sub>2</sub> capture capacity was 23.0 mmol/100 mL solvent, which represents only a 1.7% decrease compared to that obtained in Stage 1. These data confirm the mixture MEA and the IL catalyst is highly stable for long periods of time with outstanding CO<sub>2</sub> capture performance, even though the test gas stream contained 10% O<sub>2</sub>.

This impressive reproducibility of the CO<sub>2</sub> capture performance is a direct result of the stability of the catalytic CO<sub>2</sub> capture solvent system. Much milder CO<sub>2</sub> desorption temperatures (85°C), adopted in this case due to increase in CO<sub>2</sub> desorption rate by the use of the IL as a catalyst, further contributed to the stability of this solvent system. Thus, the chemical reversibility of both MEA and the catalyst can be easily realized for the tested CO<sub>2</sub> absorption and desorption temperatures (~30°C and 85°C, respectively). It should be noted that the IL catalyst is thermally stable at temperatures as high as 300°C, as shown by thermal gravimetric analysis (TGA) results in Figure 3.

Amine-modified sorbents are being used in this project as the starting materials because their reaction with CO<sub>2</sub> can be catalyzed by the IL in a similar way as shown above for amine solvent; this is because the reaction mechanism between amine and CO<sub>2</sub> are the same. These sorbents can be prepared by physically impregnating amines into porous support materials, or by chemically grafting the amine functional group onto the support surfaces, stabilizing the sorbent during regeneration. Global Thermostat, a DAC company, has patented a preparation method of using aziridine to obtain hyper-branched amino-silica (HAS) materials, resulting in high loadings of stable amine functional groups. The catalysts can be added to essentially any amine-functionalized sorbent for improved adsorption and desorption kinetics, leading to much higher CO<sub>2</sub> working capacity and much lower temperature for sorbent regeneration. This, in turn, leads to lower regeneration energy consumption and the possibility of using waste heat for desorption of these sorbents, thus significantly reducing the cost of DAC. In this project, two representative amine-modified sorbents will be selected, such as PPI- or PEI-impregnated fumed silica (SiO<sub>2</sub>).

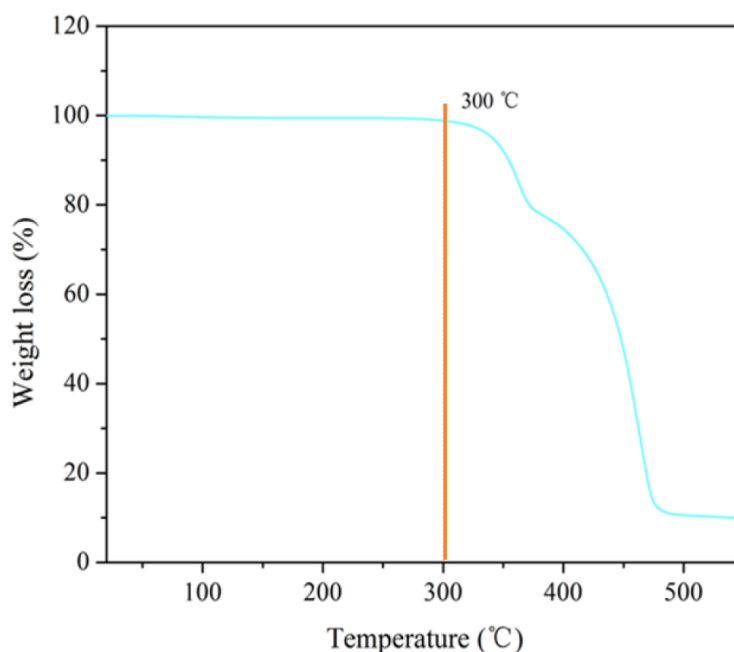


Figure 3. The TGA trace of (EMmim<sup>+</sup>)(NTF<sub>2</sub><sup>-</sup>) at 10°C heating rate.

**TABLE 1: DAC SORBENT PROCESS PARAMETERS**

| Sorbent                             | Units                          | Current R&D Value | Target R&D Value |
|-------------------------------------|--------------------------------|-------------------|------------------|
| True Density @ STP                  | kg/m <sup>3</sup>              | 1,700             | 1,700            |
| Bulk Density                        | kg/m <sup>3</sup>              | 400               | 400              |
| Average Particle Diameter           | mm                             | 0.1 – 0.2         | 0.1 – 0.2        |
| Particle Void Fraction              | m <sup>3</sup> /m <sup>3</sup> | N/A               | N/A              |
| Packing Density                     | m <sup>2</sup> /m <sup>3</sup> | 2,000 – 3,000     | 2,000 – 3,000    |
| Solid Heat Capacity @ STP           | kJ/kg-K                        | 1.6               | 1.6 – 2.0        |
| Crush Strength                      | kg <sub>f</sub>                | N/A               | N/A              |
| Attrition Index                     | -                              | N/A               | N/A              |
| Thermal Conductivity                | W/(m-K)                        | 0.2 – 0.3         | 0.2 – 0.3        |
| Manufacturing Cost for Sorbent      | \$/m <sup>3</sup>              | 41,000            | 40,000           |
| <b>Adsorption</b>                   |                                |                   |                  |
| Pressure                            | bar                            | 1 – 1.1           | 1 – 1.1          |
| Temperature                         | °C                             | 45                | 45               |
| Equilibrium Loading                 | g mol CO <sub>2</sub> /kg      | 1.1 – 1.6         | 1.1 – 1.6        |
| Heat of Adsorption                  | kJ/mol CO <sub>2</sub>         | 80                | 80               |
| CO <sub>2</sub> Adsorption Kinetics | gmol/time                      | 1.0               | 2.0              |
| <b>Desorption</b>                   |                                |                   |                  |
| Pressure                            | bar                            | 0.9               | 0.9              |
| Temperature                         | °C                             | 100 – 120         | 85               |
| Equilibrium CO <sub>2</sub> Loading | g mol CO <sub>2</sub> /kg      | 0.2               | TBD              |
| Heat of Desorption                  | kJ/mol CO <sub>2</sub>         | 80                | 80               |
| CO <sub>2</sub> Desorption Kinetics | gmol/time                      | N/A               | 3.0              |

### Definitions:

**STP** – Standard Temperature and Pressure (15°C, 1 atm).

**Sorbent** – Adsorbate-free (i.e., CO<sub>2</sub>-free) and dry material as used in adsorption/desorption cycle.

**Manufacturing Cost for Sorbent** – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

**Adsorption** – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

**Desorption** – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

**Pressure** – The pressure of CO<sub>2</sub> in equilibrium with the sorbent. If the vapor phase is pure CO<sub>2</sub>, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO<sub>2</sub>.

**Packing Density** – Ratio of the active sorbent area to the bulk sorbent volume.

**Loading** – The basis for CO<sub>2</sub> loadings is mass of dry, adsorbate-free sorbent.

**Kinetics** – A characterization of the CO<sub>2</sub> adsorption/desorption trend with respect to time, as complete in the range of time as possible.

**Flow Arrangement/Operation** – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

**Estimated Cost** – Basis is kg/hr of CO<sub>2</sub> in CO<sub>2</sub>-rich product gas; assuming targets are met.

**Atmospheric Air Feed-Gas Assumptions** – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

| Pressure  | Composition     |                  |                |                |      |                 |                 |
|-----------|-----------------|------------------|----------------|----------------|------|-----------------|-----------------|
|           |                 |                  | vol%           |                |      | ppmv            |                 |
| 14.7 psia | CO <sub>2</sub> | H <sub>2</sub> O | N <sub>2</sub> | O <sub>2</sub> | Ar   | SO <sub>x</sub> | NO <sub>x</sub> |
|           | 0.04            | variable         | 78.09          | 20.95          | 0.93 | trace           | trace           |

**TABLE 2: DIRECT AIR CAPTURE ECONOMICS**

| Economic Values         | Units                    | Current R&D Value | Target R&D Value |
|-------------------------|--------------------------|-------------------|------------------|
| Cost of Carbon Captured | \$/tonne CO <sub>2</sub> | 143               | 100              |
| Cost of Carbon Avoided  | \$/tonne CO <sub>2</sub> | —                 | —                |
| Capital Expenditures    | \$/tonne CO <sub>2</sub> | 52                | 52               |
| Operating Expenditures  | \$/tonne CO <sub>2</sub> | 91                | 48               |

#### Definitions:

**Cost of Carbon Captured** – Projected cost of capture per mass of CO<sub>2</sub> captured under expected operating conditions.

**Cost of Carbon Avoided** – Projected cost of capture per mass of CO<sub>2</sub> avoided under expected operating conditions.

**Capital Expenditures** – Projected capital expenditures in dollars per tonne of CO<sub>2</sub> captured.

**Operating Expenditures** – Projected operating expenditures in dollars per tonne of CO<sub>2</sub> captured.

#### technology advantages

- Platform technology for enhancing performance of all amine-based CO<sub>2</sub> DAC systems.
- Catalyst can be added to any amine-based sorbents or solvents for improved sorption and desorption kinetics.
- Low-risk technology that can be applied to existing low-pressure-drop contactor designs.

- The sorbent-based process enables a reduction in the energy required for sorbent regeneration and increased sorbent lifetime/stability due to operation at lower desorption temperatures.

## R&D challenges

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- Developing an IL catalyst that can be added to amine-doped DAC sorbents to increase desorption kinetics.
- Developing sorbents with low regeneration temperature and low regeneration energy for direct air capture of CO<sub>2</sub>.

## status

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Susteon's patented IL catalyst has demonstrated improvement in CO<sub>2</sub> adsorption capacity of amine sorbents by approximately 50%, with much longer breakthrough times. This catalyst-sorbent combination also improved desorption rate by up to 80%. Susteon also successfully scaled-up catalyst production to kilogram scale. A preliminary technology maturation plan (TMP) was completed, DAC process cost parameters were analyzed, the catalyst synthesis recipe was defined, and quality control procedures were established. Current work involves screening synthesized sorbents through testing at DAC operating conditions.

## available reports/technical papers/presentations

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James Zhou, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO<sub>2</sub>," Project kickoff meeting presentation, Pittsburgh, PA, October 2020. <http://www.netl.doe.gov/projects/plp-download.aspx?id=11092&filename=Low+Regeneration+Temperature+Sorbents+for+Direct+Air+Capture+of+CO2.pdf>.

James Zhou, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO<sub>2</sub>," Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. [https://netl.doe.gov/sites/default/files/netl-file/21DAC\\_Zhou.pdf](https://netl.doe.gov/sites/default/files/netl-file/21DAC_Zhou.pdf).

James Zhou, Maohong Fan, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO<sub>2</sub>," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. [https://netl.doe.gov/sites/default/files/netl-file/21CMOG\\_CDRR\\_Zhou.pdf](https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Zhou.pdf)