Front Side Copper Metallization Paste for Silicon Solar Cells

Cooperative Research and Development Final Report

CRADA Number: CRD-23-23799

NREL Technical Contact: Pauls Stradins

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Office of Energy Efficiency & Renewable Energy
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Technical Report
NREL/TP-5K00-96760
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NOTICE

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Cooperative Research and Development Final Report

Report Date: July 28, 2025

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the CRADA final report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Bert Thin Films

CRADA Number: CRD-23-23799

CRADA Title: Front Side Copper Metallization Paste for Silicon Solar Cells

Responsible Technical Contact at NREL:

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Name and Email Address of POC at Company:

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Sponsoring DOE Program Office(s):

Office of Energy Efficiency and Renewable Energy (EERE), Solar Energy Technologies Office

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	$55,000.00
TOTALS	$55,000.00

Executive Summary of CRADA Work:

Adoption and testing of copper (Cu) metallization pastes on existing research and development (R&D) or production lines is hindered by the perceived idea that Cu will contaminate the equipment. The objective of this work is to prove if Cu from the pastes will contaminate and degrade the silver metallized cells being produced in the same firing furnace.

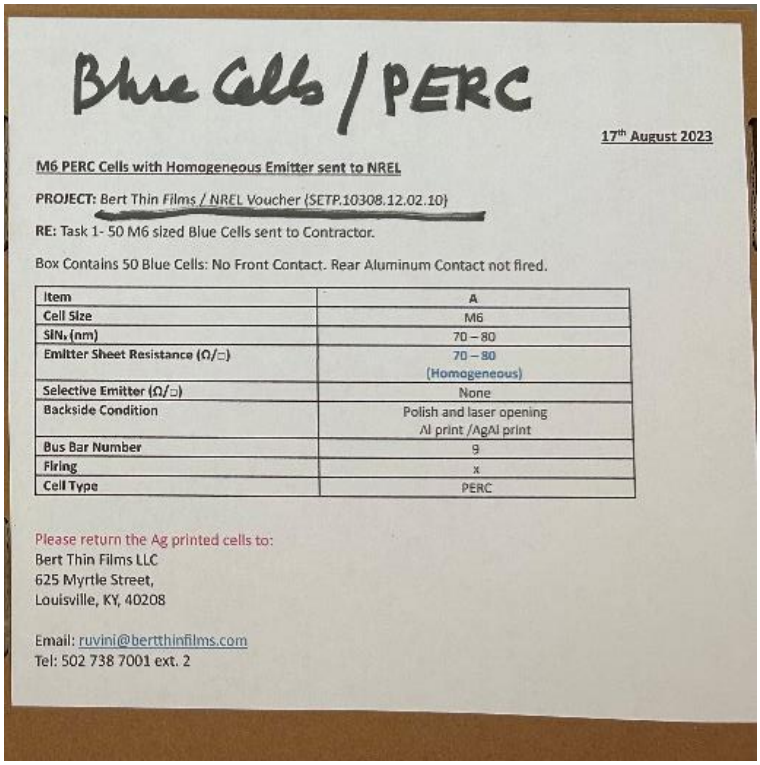
CRADA benefit to DOE, Participant, and US Taxpayer:

Uses the laboratory's core competencies

Summary of Research Results:

Task 1: The Participant will provide 50 M6 sized Blue cells to the Contractor.

The contractor received 50 M6 sized blue cells in Aug 2023.



Blue Cells / PERC

17th August 2023

M6 PERC Cells with Homogeneous Emitter sent to NREL

PROJECT: Bert Thin Films / NREL Voucher (SETP.10308.12.02.10)

RE: Task 1- 50 M6 sized Blue Cells sent to Contractor.

Box Contains 50 Blue Cells: No Front Contact. Rear Aluminum Contact not fired.

Item	A
Cell Size	M6
SiN_x (nm)	70 – 80
Emitter Sheet Resistance (Ω/□)	70 – 80 (Homogeneous)
Selective Emitter (Ω/□)	None
Backside Condition	Polish and laser opening Al print /AgAl print
Bus Bar Number	9
Firing	x
Cell Type	PERC

Please return the Ag printed cells to:
Bert Thin Films LLC
625 Myrtle Street,
Louisville, KY, 40208

Email: ruvini@bertthinfilms.com
Tel: 502 738 7001 ext. 2

Figure 1. A packet of 50 Blue PERC cells shipped from BERT Thin Films to NREL

Task 2: The Contractor will print a suitable Ag paste on the front of the Blue Cells. The Contractor will retain a 3rd of the cells to act as the control group and send the remainder to the Participant.

The contractor printed Ag paste on the front of the Blue cells.

Task 3: The Participant will print 50 M6 sized Blue cells with their proprietary Cu paste.

The contractor received the Cu paste printed Blue cells in Feb 2024.

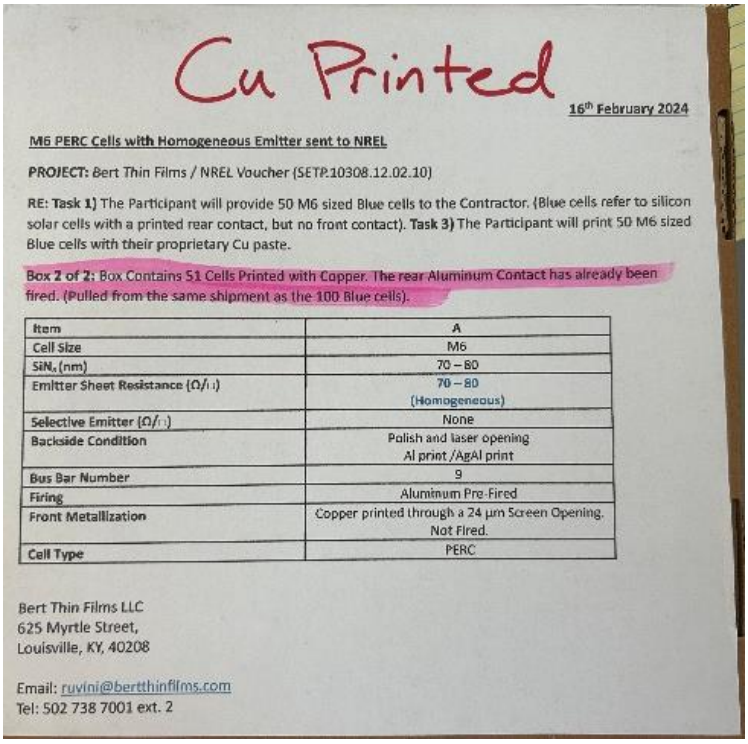


Figure 2. A packet of 50 Blue PERC cells with Cu paste printed shipped from BERT Thin Films to NREL

Task 5: The Contractor will fire the control group (F1) in a rapid thermal processing (RTP) unit.

The contractor printed Ag paste on the front side of the M6 cells and fired three of them in a RTP unit at different firing peak temperatures (i.e. 740 C, 760 C and 780 C) to determine an optimal firing profile for these cells. The sample fired at 760 C was found to give the best efficiency as shown below.

Table 1. JV parameters of cells with Ag paste front grid fired at 740 C, 760 C and 780 C

	Fired at 740 C	Fired at 760 C	Fired at 780 C
Voc (mV)	665	663	656
Jsc (mA/cm2)	39	39	38
FF (%)	77.3	80.9	80.3
Eff (%)	20.2	20.9	20.2

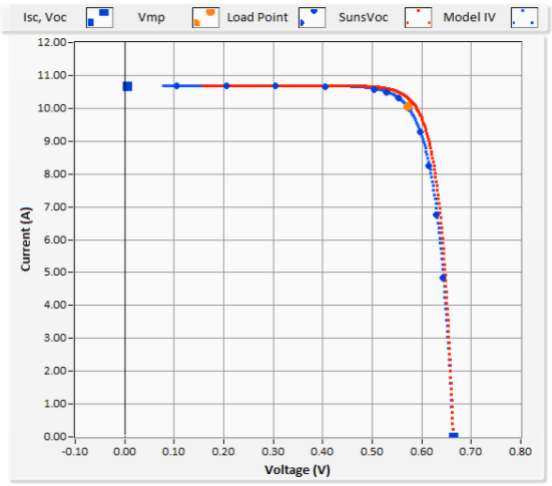


Figure 3. JV of cell with Ag paste printed on the front side of the cell and fired at 760 C

Task 4: The Participant will laser scribe the Cu printed cells, and the Ag printed cells provided by the Contractor into approximately 4 × 4 cm2 sections.

At the time of writing the statement of work (SOW), the Contractor was unsure whether copper (Cu) metallized cells could be fired in their facilities, due to the possibility of Cu contaminating their primary RTP unit. Therefore, the SOW for this project was written assuming that samples would have to be fired at the Participant's facilities. At the time, the Participant was only able to fire 4 × 4 cm^2 sections. In May 2023, the Contractor confirmed that they had a second RTP unit that could be possibly adapted for this project. Consequently 50 "Blue" PERC cells were sent to NREL in August 2023 to start printing the silver (Ag) metallized cells to be used in this project. In February 2024, an additional 50 "Blue" cells and 51 PERC cells screen printed with the participant's Cu paste were sent to the Contractor. Table 2 shows the structure of the cells sent for the completion of this project. Metallization screen designs and firing profiles for the Cu pastes were also provided to the Contractor during this project. At this point, all firing was anticipated to be completed at the Contractor's facilities using the larger cells.

Table 2. Structure of Passivated Emitter Rear Contact (PERC) and number of cells sent to the Contractor.

Item	Blue Cells	Cu Metallized Cells
Cell Size	M6 (166 mm × 166 mm)	M6 (166 mm × 166 mm)
Front Contact	No metallization	Cu contacts screen printed by the Participant and not fired.
SiNx (nm)	70 – 80	70 – 80
Emitter Sheet Resistance (Ω/□)	70 – 80	70 – 80
Selective Emitter (Ω/□)	(Homogeneous Emitter)	(Homogeneous Emitter)
Backside Condition	Polish and laser opening Al printed /AgAl printed Al not fired	Polish and laser opening Al printed /AgAl printed Al pre-fired
Bus Bar Number	9	9
Cell Type	PERC	PERC
Set ID	A	A
No. of Cells Sent to the Contractor.	100	51

Note on samples and RTP used for Task 5 and 6 below

Task 5, and 6 are performed on cells with separate groups from F1 to F6 and the description of these cells and the RTP unit used for each group are listed in the table below.

RTP-1 is the main unit used for different Si group projects and this RTP has not been exposed to Cu or other contaminants that can lower the performance of the Si cells. This RTP was used in this project only to obtain an optimal firing profile of the Ag paste printed cells.

RTP-2 is an old spare unit that was repurposed to fire Cu metallized cells to avoid contaminating RTP-1. Similar firing profile to RTP-1 was developed with peak firing temperature of 750 C and most of the Ag paste printed cells and all of the Cu paste printed cells are fired in RTP-2.

Table 3. Type of metal paste, RTP and number of samples used for each sample group for firing

Sample Group #	Type of front grid paste	Purpose	RTP used	# of samples
F1	Ag	Group used to find an optimized firing profile	RTP – 1	6
F2	Ag	Control group - Ag group before firing Cu metallized samples	RTP - 2	21
F3	Cu	1st Cu metallized samples fired	RTP - 2	25
F4	Ag	Ag group after firing Cu metallized samples	RTP - 2	21
F5	Cu	2nd Cu metallized samples fired	RTP - 2	25
F6	Ag	Ag group after firing Cu metallized samples	RTP - 2	21

Task 5: The Contractor will perform electrical characterization on Ag metallized sections from Groups F1, F2, F4 and F6.

The Ag paste printed cells were measured using a Sinton Flash Tester and results for different groups of cells are shown below. Ideally, we would compare the bulk lifetime of the cells that were fired before and after the furnace was exposed to Cu metallized cells, however, the R^2 fit for the lifetime provided by the flash tester was low for most of the samples. In some cases, bulk lifetime of the cells was not provided. Thus, here we compare Voc values to see if the performance of Ag metallized cells decreased after Cu metallized cells were fired in the same furnace.

Please note that F1 group was fired in RTP-1 whereas F2, F4 and F6 groups were fired in RTP-2. F2 were fired before the Cu metallized cells were introduced into RTP-2. F4 cells were fired after 25 Cu metallized cells were fired and F6 cells were fired after an additional 25 Cu metallized cells were fired.

From the graph below, the Voc of the cells in the F3 and F4 are comparable to the those of F2 and F1. F2 group has a spread in Voc and additional analysis is required to understand the spread of Voc in this group. It is interesting that cells in F6 group have slightly lower Voc values compared to those in the F4 group, however, the values are still within +/- 2 mV. Additional study with more samples is needed to see if this trend will continue as more and more Cu metallized cells are fired in the chamber. For the number of cells used for this study, firing the Ag metallized cells in the same chamber where the Cu metallized cells had been fired has not significantly decreased the performance of the Ag metallized cells.

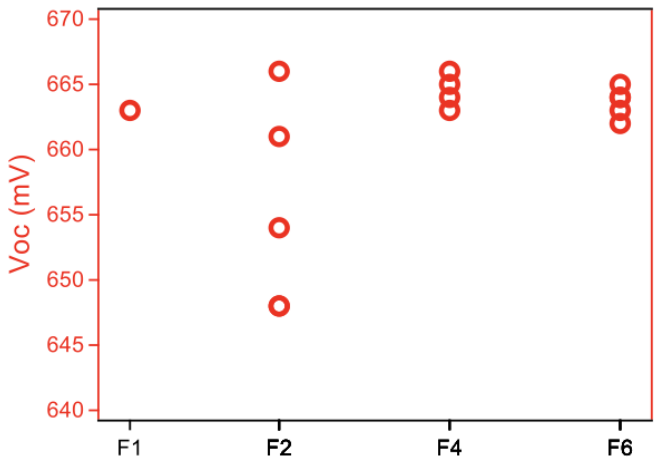


Figure 4. Measured Voc of the solar cells from Group F1, F2, F3 and F6

Task 6: The Contractor will perform analytical characterization on Ag metallized sections from Groups F1, F2, F4 and F6.

PL imaging and characterization were done on the samples without the front grids from F2, F4, and F6 groups to track the gain in Voc of the samples before and after firing. The range of gain in Voc for all the groups are similar with an average Voc gain of 21.3 mV for F2, 22.9 mV for F4 and 19.6 mV for F6. It is interesting that samples in F6 group again have a slightly lower gain in Voc values compared to those in the F4 group. Additional study with more samples is needed to see if this trend will continue as more and more Cu metallized cells are fired in the same chamber. For the number of samples used for this study, the cells in F2, F4 and F6 gain similar Voc after firing.

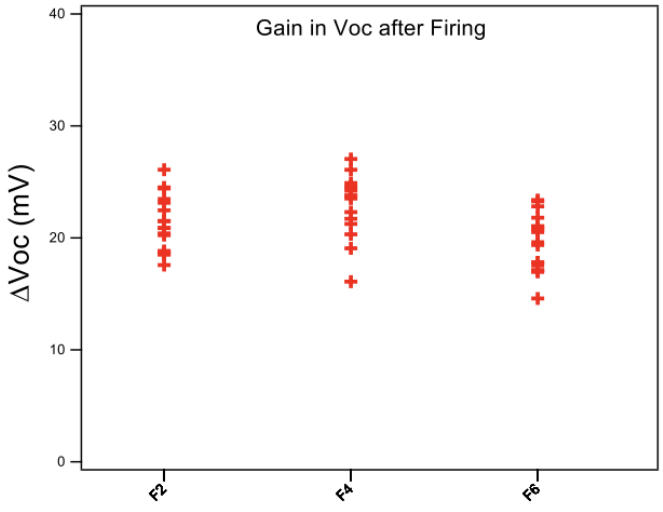


Figure 5. ΔVoc of cells extracted from PL Intensity before and after firing

Task 5: The Contractor will thermally stress the Ag metallized sections from groups F1, F2, F3 and F4.

This task was not performed as much of the funding had to be spent on repurposing the RTP-2 unit needed to complete the firing process of cells from F2 to F6. Please see task 9 (additional tasks section).

Task 6: The Contractor will repeat electrical characterization on the thermally stressed Ag metallized sections from Groups F1, F2, F4 and F5.

This task was not performed as much of the funding had to be spent on repurposing the RTP-2 unit needed to complete the firing process of cells from F2 to F6. Please see task 9 (additional tasks section).

Task 7: The Contractor will repeat analytical characterization on Ag metallized sections from Groups F1, F2, F4 and F5.

This task was not performed as much of the funding had to be spent on repurposing the RTP-2 unit needed to complete the firing process of cells from F2 to F6. Please see task 9 (additional tasks section).

Task 8: The Contractor will compare the results before and after the accelerated aging tests to determine whether Cu contamination can be observed in the Ag metallized cells from each of the groups.

This task was not performed as much of the funding had to be spent on repurposing the RTP-2 unit needed to complete the firing process of cells from F2 to F6. Please see task 9 (additional tasks section).

Task 9: Additional Tasks

In order to complete this CRADA work, a separate RTP (RTP-2) was needed to ensure that Cu paste printed cells will not contaminate the main RTP chamber (RTP-1) used for other Si projects. Much of the work for this CRADA was delayed mainly due to the maintenance, modification and relocation of RTP-2 so that the unit can be repurposed for this project. The repair and modification of the unit involves three main areas: process cooling water (PCW), replacement of the lamps, decontamination and repair of quartz chamber and modification of the quartz wafer tray.

PCW is an essential part of the operation of RTP since the unit will not operate without enough flow of cooling water. Our inspections showed that the line inside the unit was clogged in some areas due to metal flaking inside the RTP and corrosion from PCW (images below). Some parts were worn and O-rings were also damaged.

Figure 6. (Left) Corroded particles and metal flakes from PCW (Mid and Right) Worn out and damage parts and O-ring

We flushed the lines, replaced the worn parts, performed leak check and tested the PCW channel pressure over 24 hours. The exhaust line was also clogged, and the gas supply line was also not connected to the chamber. The exhaust line was renewed, and the gas supply line was also re-connected to the chamber for proper operation of the unit.

The lamps inside the unit were either broken or not operating properly and thus, all 21 lamps were replaced with 3 – month old used lamps from RTP-1. The lamps' function and intensity were checked after the replacement.

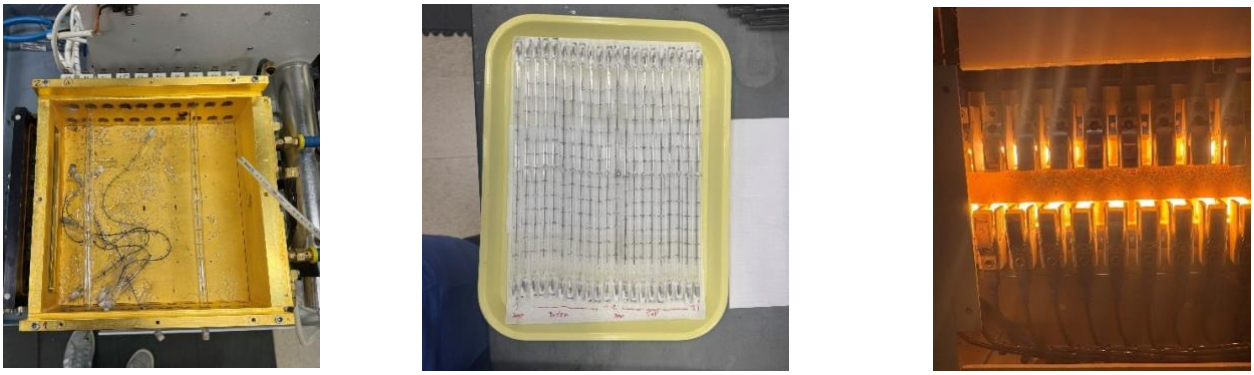


Figure 7. (Left) Lamps broken inside the RTP-2 (Mid) 3-month old used lamps from RTP-1 (Right) Lamps function and intensity check after replacement

The quartz chamber was also cleaned with different chemicals to decontaminate the chamber; however, cracks started to form inside the chamber during the decontamination process due to existing micro-cracks. The chamber was sent to Allen Scientific Glass Inc. for repair. Quartz tray was also modified to fit the wafer and the renewed thermocouple setup.

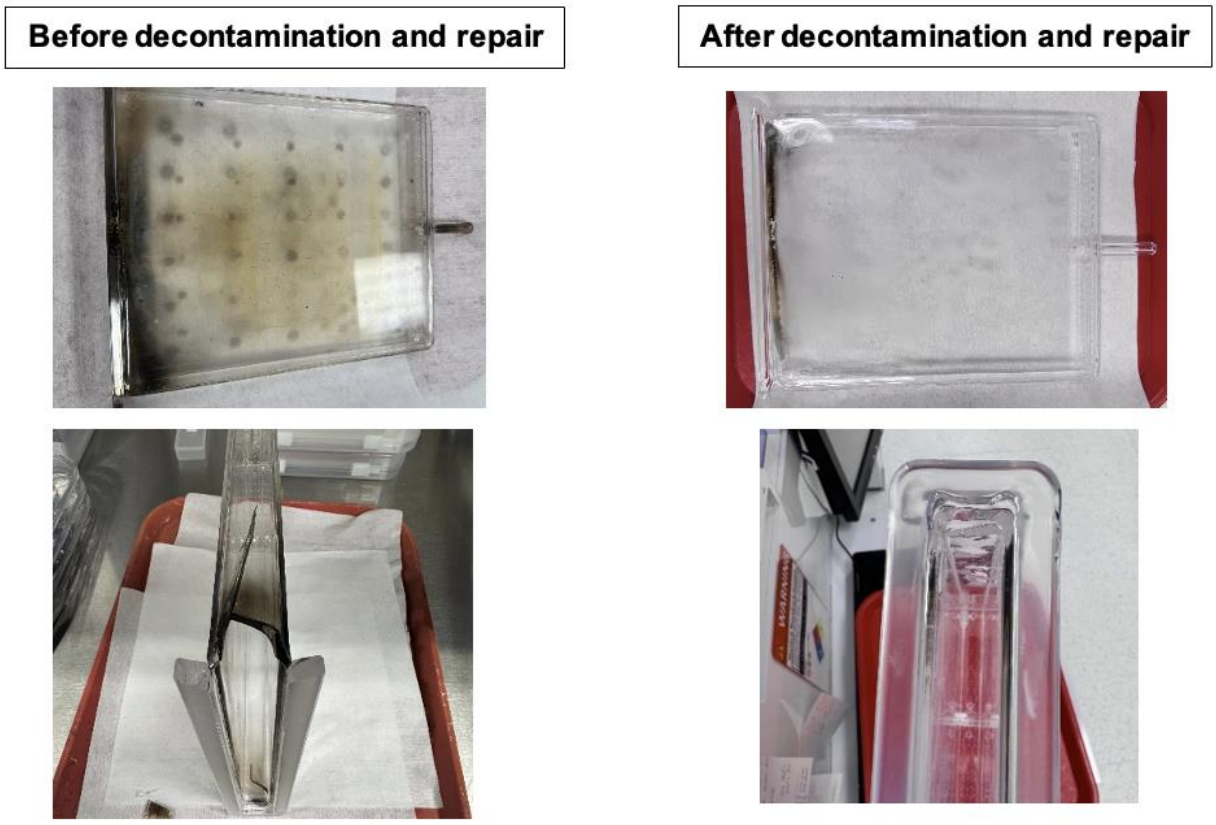


Figure 8. Quartz chamber (Left) before and (Right) after decontamination and repair

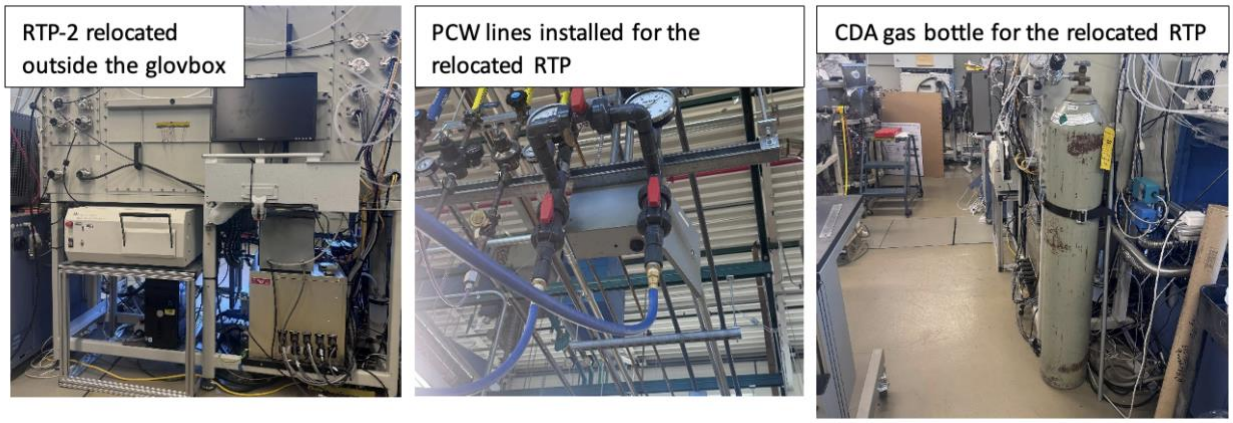


Figure 9. New location of the RTP-2 with PCW lines and CDA gas bottle installed and reconnected

Originally, RTP-2 was located in a glovebox but after the repair, it had to be relocated out of the glovebox as some other work was being done inside that glovebox. The relocation required decontamination and cleaning of the surface of the unit, installation of the PCW lines, exhaust lines, house CDA purge lines, CDA gas bottle and a RTP stand. Main power for the unit, PC and the monitor rack also had to be relocated.

Task 10: CRADA Final Report

This report serves to meet the requirement for the CRADA Final Report with preparation and submission in accordance with the agreement's Article X.

Subject Inventions Listing:

None.

ROI#:

None.