Proposed Rule 1435 – Control of Toxic Air Contaminant Emissions from Metal Heating Operations

WORKING GROUP MEETING #2

May 18, 2023
9:00 AM (PST)
South Coast AQMD
Diamond Bar, CA

Join Zoom Webinar Meeting - from PC or Laptop
https://scaqmd.zoom.us/j/96825066787
Zoom Webinar ID: 968 2506 6787
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South Coast AQMD

AGENDA

- Background
- South Coast AQMD Emissions Testing and Sampling
- Facility Survey
- CE-CERT Study
- Rule Development Process
- Next Steps

BACKGROUND

Toxic Air Contaminants

- Hexavalent chromium is a toxic air contaminant that is a potent carcinogen
  - Primarily produced by industrial processes
  - Long-term inhalation of hexavalent chromium can increase the risk of developing lung and nasal cancers
- Other toxic metals such as cobalt or nickel also have adverse health affects

Health Effects of Hexavalent Chromium

A fact sheet by
CalEPA's Office of Environmental Health Hazard Assessment
November 9, 2016

OEHHA

What is hexavalent chromium?

Hexavalent chromium, also known as chromium 6 (Cr6), is the toxic form of the metal chromium. While some less toxic forms of chromium occur naturally in the environment (soil, rocks, dust, plants, and animals), Cr6 is mainly produced by industrial processes.

Cr6 is used in:

- Electroplating
- Stainless steel production and welding
- Pigments and dyes
- Surface coatings
- Leather tanning

How are people exposed to Cr6?

Humans are exposed to Cr6 by:

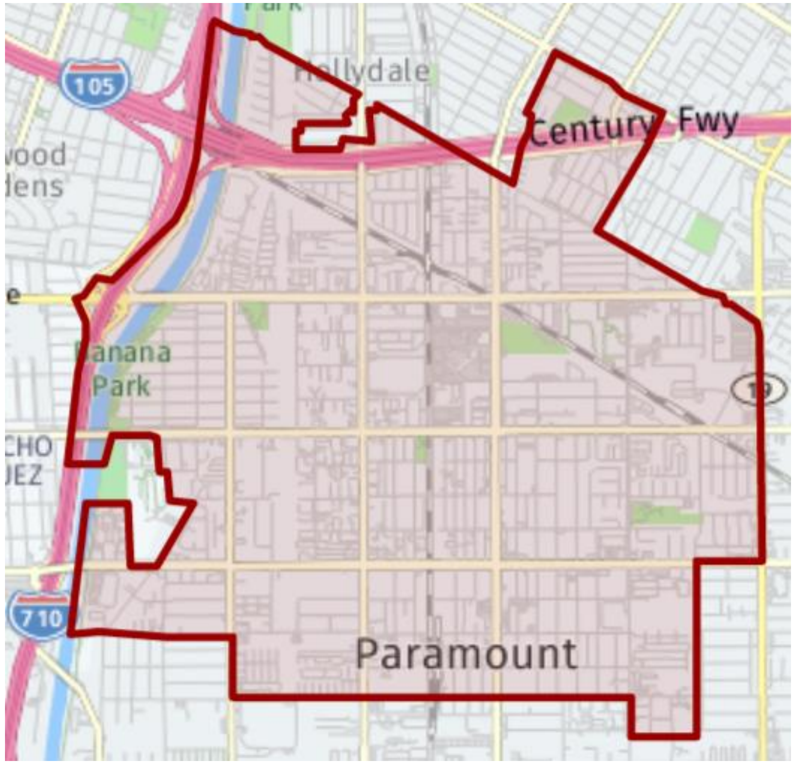
- Inhalation of aerosols or particles
- Ingestion (eating and drinking)
- Skin contact

Cr6 may occur as aerosols or particulate matter in air. These can be inhaled directly or ingested after they land on soil or water. Contact with soil containing Cr6 may transfer to the hands and then to the mouth. Young children put their hands in their mouths more frequently than adults. For this reason, young children are more likely to consume contaminated soil. Children are also more active outdoors and they may have more contact with contaminated soil.

One form of Cr6, chromic acid, is created as a mist during electroplating. Workers and bystanders may inhale the mist. Chromic acid can also be absorbed through the skin. In addition, chromic acid deposited on the skin can be ingested through hand-to-mouth activities, such as eating.

Background

- Elevated levels of hexavalent chromium were observed during the 2016 monitoring efforts in Paramount
- Further investigation identified a heat treating facility and forging facilities as sources of hexavalent chromium
- Proposed Rule 1435 will address toxic air contaminant emissions sources from metal heating



Working Group Meeting #1 Summary

- Working Group Meeting #1 held in August 2019
  - Provided testing and sampling results that showed presence of hexavalent chromium from multiple emission sources at heat treating and forging facilities
  - Informed stakeholders of planned UC Riverside’s Center for Environmental Research and Technology (CE-CERT) testing to evaluate emissions of hexavalent chromium from metal heating
  - CE-CERT testing and PR 1435 rule development was paused during the pandemic

Rulemaking Activities To Date

CE-CERT Study	Site Visits	Working Group Meeting #1	Facility Universe	Survey
• Contracted with CE-CERT in 2018 to study the formation of hexavalent chromium in furnaces • Final report available in December 2022	• 12 site visits at heat treating, forging, and other metalworking facilities	• Held in 2019 • Discussed background information and potential scope of rule	• Identified nearly 140 facilities that operate metal heating furnaces through South Coast AQMD database and internet searches	• Distributed information-gathering survey to all identified facilities in 2020

Working Group Meeting #2 Topics

1

South Coast AQMD Emissions Testing and Sampling

2

Facility Survey

3

CE-CERT Study

1

South Coast AQMD Emissions Testing and Sampling

South Coast AQMD Testing and Sampling

- Five facilities evaluated (2016-2017)
  - One heat treating facility
  - Four forging facilities
- Elevated hexavalent chromium concentrations were detected at several furnaces across all five facilities
- Sampling at heat treating facility’s quench tanks and outdoor storage area also found hexavalent chromium

Results for Heat Treating Furnaces

- Emissions tests were conducted on three furnaces
- Data showed high emissions of hexavalent chromium

Emission Screening Test				
Furnace	**Alloy**	**% Chromium Content**	**Temperature (°F)**	**Cr^{+6} Emission Concentrations (ng/m^3)**
#3	Inconel	14 - 31	2100	**376**

<table>
<tr><th colspan="6">Source Tests</th></tr>
<tr><th>Furnaces</th><th>Alloy</th><th>% Chromium Content</th><th>Temp (°F)</th><th>Cr^{+6} Emission Concentrations (ng/m^3)</th><th>Cr^{+6} Mass Emissions (mg/hr)</th></tr>
<tr><td rowspan="2">#11</td><td>Chromium alloy</td><td>% not given</td><td>1250</td><td>9564</td><td>8.0</td></tr>
<tr><td>Titanium</td><td>N/A</td><td>1250</td><td>3224</td><td>4.2</td></tr>
<tr><td rowspan="3">#14</td><td>Chromium alloy</td><td>% not given</td><td>1800</td><td>1670</td><td>6.6</td></tr>
<tr><td>Titanium</td><td>N/A</td><td>1800</td><td>Indeterminate*</td><td>N/A</td></tr>
<tr><td>Empty</td><td>N/A</td><td>1800</td><td>Indeterminate*</td><td>N/A</td></tr>
</table>

* Exhaust concentrations were equal to or below background concentrations

Results for Bulk Sampling

Sampling Location	Sampled Materials	Cr^{+6} Concentrations
Outdoor Storage Area	Metal dust	**190 ppm**
Treated Titanium Workpiece	Scale scraping	**0.018 ppm**

- Metal dust sample collected in storage area showed high hexavalent chromium
- Metal dust likely originated from heat treated workpiece surfaces
  - Workpiece surfaces took on a scaly, rust-like appearance after heat treating, indicative of oxidization
  - Forced air cooling of workpieces created airborne dust
  - Insufficient housekeeping resulted in dust buildup in the facility
- Sample from titanium workpiece found low concentration of hexavalent chromium

Results for Quench Tanks

Sampling Location	Sampled Material	Cr^{+6} Concentrations
Water Quench Tank	Quench solution	**46 mg/L**
• 1 ft above surface	Fugitive emissions	**638 ng/m^3**
Oil Quench Tank	Quench solution	**0.005 mg/L**
• 1 ft above surface	Fugitive emissions	**130 ng/m^3**

- Quench water contained hexavalent chromium
  - Open circuit cooling tower was circulating the quench water and releasing airborne water droplets
- Quench oil solution contained very small amounts of hexavalent chromium
  - High concentrations detected above tank surface may have been influenced by ambient dust in facility

Summary of Heat Treating Facility Results

- Emissions tests showed that heat treating furnaces produced elevated levels of hexavalent chromium
- Two additional sources of hexavalent chromium emissions identified:
  1. Droplets of water from water quench bath became airborne in the water quench cooling towers
  2. Dust from oxidized workpiece surfaces disturbed by forced air cooling and other activities

Mitigation Efforts at Heat Treating Facility

- Enclosed buildings to create permanent total enclosures (PTEs) and installed baghouse controls and ultra-low particulate air (ULPA) filters on building ventilation exhaust
  - All furnaces and quenching now operate within PTEs
- Quench tank modifications
  - Cooling tower removed – quench water is now naturally cooled
  - Quench water is regularly monitored and ferrous sulfate is periodically added to reduce hexavalent chromium
- Discontinued fan cooling
  - Air cooling of workpieces is conducted indoors
- Enhanced housekeeping – facility is regularly vacuumed and swept to avoid dust buildup

Emissions Testing at Forging Facilities

- Conducted emissions screening tests to quantify hexavalent chromium from seven forging furnaces
- Forging furnaces are used to heat metals to a temperature below the melting point at which the metals are malleable
  - The heated metals are then forged and manipulated to the desired shapes and sizes
- Operating temperature ranges may be hotter than those of heat treating furnaces

Test Results from Forging Furnaces

Facility	Furnaces	Alloy	% Chromium	Temperature (°F)	Cr^{+6} (ng/m^3)
Facility A	Furnace 1A	Waspaloy	18-21	1900	137
Facility B	Furnace 1B	300/400 series stainless steel	10-30	2192	34.6
	Furnace 2B	300/400 series stainless steel	10-30	2252	49.3
	Furnace 3B	Titanium	N/A	1750	82.3
Facility C	Furnace 1C	Titanium	N/A	1725	Non-Detectable & 7.04 *(at 2 separate stacks)*
	Furnace 2C	Titanium	N/A	1725	24,500 *****
Facility D	Furnace 1D	Workpieces w/ 15.5% chromium	15.5	2050	2,080

* Furnace used a large stainless steel rotating table to rotate workpieces

Emissions from Furnace 2C

- Very high hexavalent chromium emissions from Furnace 2C
  - Titanium workpieces were not expected to have significant levels of chromium
  - Large stainless steel (chromium-containing alloy) rotating table was present in the furnace

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	Furnace 2C	Titanium	N/A	1725	24,500 *
Facility D	Furnace 1D	Workpieces w/ 15.5% chromium	15.5	2050	2,080

- Staff believes the stainless steel rotating table was the source of chromium

Takeaways from Testing and Sampling Results

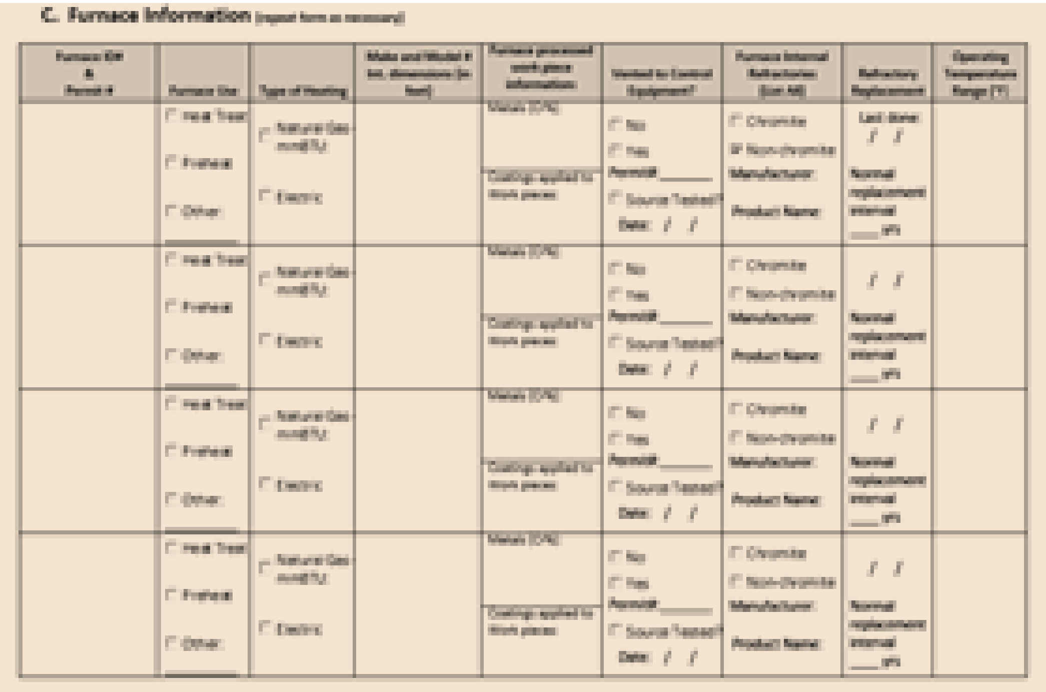
- Hexavalent chromium emissions observed from furnaces
  - Higher furnace emissions did not clearly correlate with higher chromium content or furnace temperatures
- Quench tanks and fugitive metal dust may be sources of hexavalent chromium emissions
- Insufficient housekeeping contributed to emissions
- More information was needed in order to identify factors behind formation of hexavalent chromium in metal heating furnaces

2

FACILITY SURVEY

Facility Survey

- Objective: to gather information about equipment, operations, general industry practices, and approaches to housekeeping
- Distributed survey to 137 facilities via email and direct mailing in January 2020



Responses Summary

- A response rate of 20%
  - 28 facilities returned completed surveys
- 24 of the 28 completed surveys identified the industries served
  - Mostly aerospace, others include commercial, military, oil and gas, and medical
- 21 facilities use metal racks to support workpieces in furnaces during the heating process

Responses Summary *(continued)*

- 292 furnaces identified by the survey
  - Number of furnaces ranged from 1 to 63 per facility
  - Majority of furnaces operate at temperatures greater than 1500°F
  - Most furnaces heat chromium-containing metal alloys, but amount of chromium varies greatly

Operating Temperature Range	Number of Furnaces
Less than 1100°F	67
1100°F – 1500°F	22
Greater than 1500°F	169
Not Provided	34
Total	292

Maximum % of Cr Present in Alloys	Number of Furnaces
> 20%	79
1% - 20%	44
Unknown % (Cr is present)	58
Less than 1%	27
None	49
Not Provided	35
Total	292

Responses Summary *(continued)*

- 53 quench tanks at 16 facilities were captured in the survey
- Housekeeping schedules for furnaces, quenching areas, and other areas varied across facilities
  - Common housekeeping methods included mopping, HEPA vacuuming, and sweeping

Quench Solution	Number of Quench Tanks
Water	30
Oil	13
Other	10
Total	53

Housekeeping Frequency	Number of Facilities
Multiple times a day	4
Daily	10
Every Other Day to Weekly	6
Monthly	3
No regular schedule	4
Not listed	1
Total	28

3

CE-CERT STUDY

CE-CERT Study

- South Coast AQMD funded a study conducted by CE-CERT
- Objective was to document hexavalent chromium emissions from furnaces used to heat metal
  - Not intended to develop an emission factor
- Examined hexavalent chromium emissions resulting from heating metal to different temperatures for sustained periods of time
- California Metals Coalition provided testing materials and industry expertise
- Final Report provided to South Coast AQMD in December 2022
  - Available on PR 1435 web page: http://www.aqmd.gov/docs/default-source/rule-book/Proposed-Rules/1435/final-report-hexavalent-chromium-emissions-from-industrial-heat-treating-furnaces.pdf?sfvrsn=9

Test Materials

- Test materials consisted of:
  - Multiple punchout samples of four different metal alloys
  - Three samples of used furnace refractory material
  - Refractory reinforcing needles, racks, and trays
    - These items are often present within the furnace chamber and are manufactured with metal alloys such as stainless steel, and meant to withstand multiple rounds of heating

Test Materials *(continued)*

Metal Alloys	Chromium Content (%)
I-625	20.0 – 23.0
410	12.0
N-50	20.5 – 23.5
17-4	15.5

Refractory Material	Average Chromium Content (wt %)
R1	0.52
R2	0.16
R3	0.25

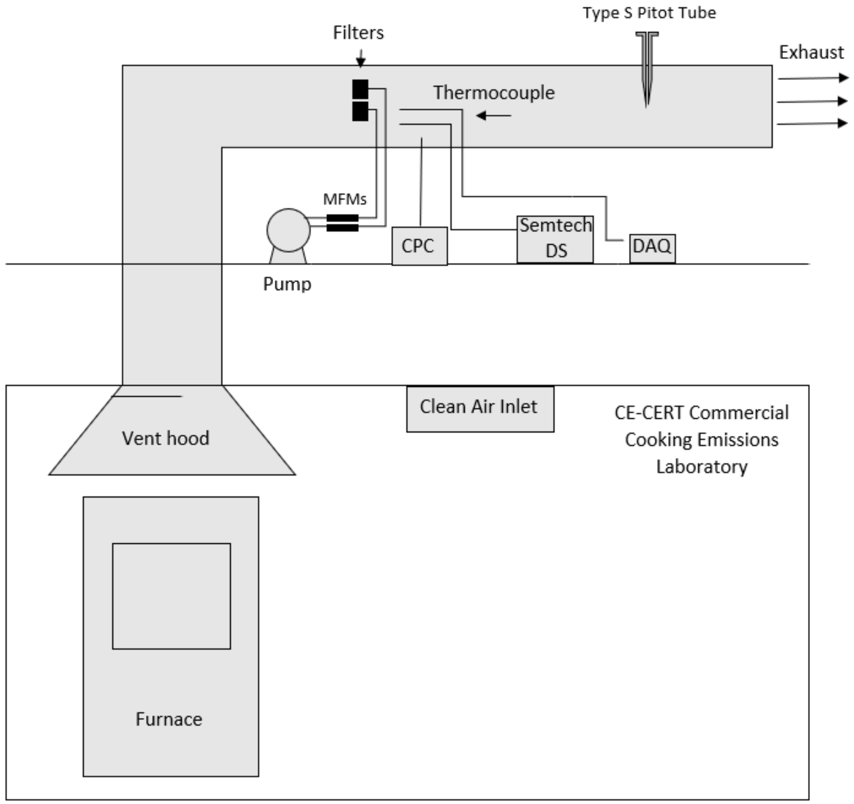
Racking/Tray/Needles Alloys	Chromium Content (%)
301 Stainless Steel	24 – 26
304 Stainless Steel	18 – 20
HR-9	19 – 21
HU Stainless Steel	17 – 21
RA 330	17 – 20

Furnace Information

MIFCO HTG-98 Gas Heat Treat Furnace

Furnace Model	HTG-98
Door Size	12”W x 8”H
Chamber Size	15”W x 13”H x 25”D
Hearth Size	11”W x 24½”L
Gas Input (BTU/hr)	350,000
Motor Rate	½ hp, 3600 rpm
Temperature Range	400°F - 2200°F
Blower Rate	90 cfm
Overall Height	72”
Floor Space	42” x 42”
Gas Connection	1”
Gas Service	1½”
Approximate Weight	1560 lbs

Sampling System and Procedure



Schematic of Sampling System

- Exhaust system used to collect samples of furnace emissions
  - Furnace was placed under an exhaust hood
  - Two cellulose filters were placed inside the duct in two separate sampling sites
    - Second sampling site is located 11 feet downstream of the first sampling site
    - Simultaneous upstream/downstream samples show consistent results, demonstrating that hexavalent chromium is not being reduced in the ducting
- Sample Collection:
  - After materials were heated in the furnace during a two-hour warm-up period at each testing temperature
  - During blank tests
- The filters were collected and delivered to South Coast AQMD laboratory for analysis

Testing Procedures

- Empty furnace was first operated ("blank test") to measure potential for hexavalent chromium emissions from the furnace
- Each material was tested at 3 or 4 different temperatures, followed by a blank test
- Furnace interior was vacuumed every day prior to testing
- Metal alloys and refractory material samples were tested at temperatures of 2100°F, 1900°F, and 1500°F
- Racking, tray, and needle materials were tested at 2100°F, 1900°F, 1500°F, as well as 800°F to better understand hexavalent chromium formation at low temperature conditions
  - New and used materials were compared to better understand how potential structural changes can affect hexavalent chromium emission rates
- Blank tests were conducted at 2100°F between the testing of different materials

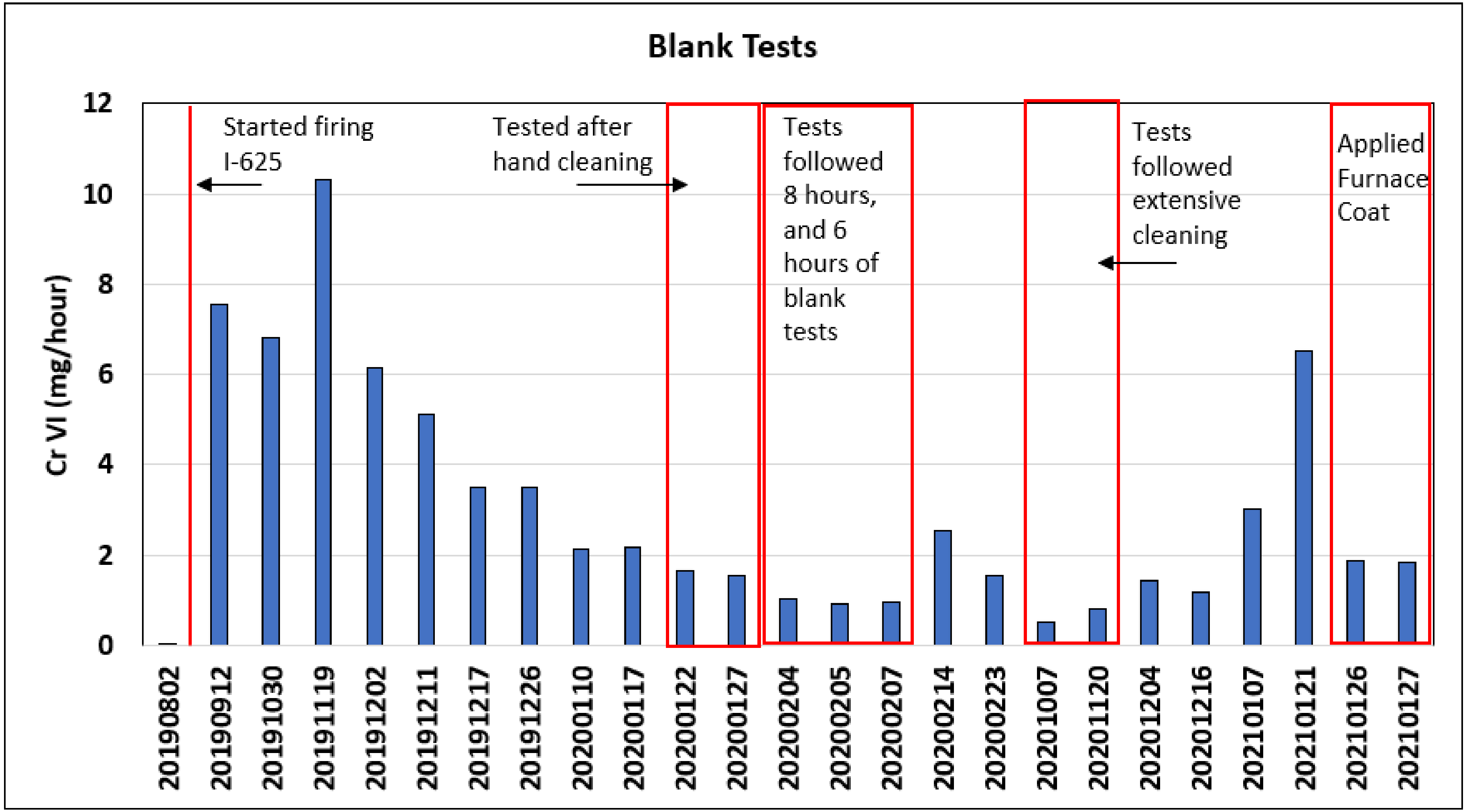
Results – Blank Tests

- Except for initial tests conducted prior to introducing samples into the furnace, the blank tests showed detected levels of hexavalent chromium emissions
- Sample tests at high temperatures may have caused the formation of hexavalent chromium-containing scale and dust which were then collected during blank tests
  - Particles accumulated in the furnace and were absorbed into the porous furnace walls and hearth bricks, and were then released during subsequent high temperature testing
  - These particles remained in the furnace and caused elevated levels of hexavalent chromium emissions even when there was nothing in the furnace
- Extensive cleaning, extended heating periods with no metals, and applying a furnace coating was shown to reduce hexavalent chromium emissions from blank tests

Results – Blank Tests *(continued)*

Key Takeaways

- Initial blank results show no hexavalent chromium emissions, proving that the furnace itself is not a source
- Blank results after various cleaning procedures show lower emissions, demonstrating that the source of blank emissions is from previous alloy heating



Page 20, Figure 4 – Hexavalent chromium emissions obtained from blank experiments

Results – Metal Alloy Samples

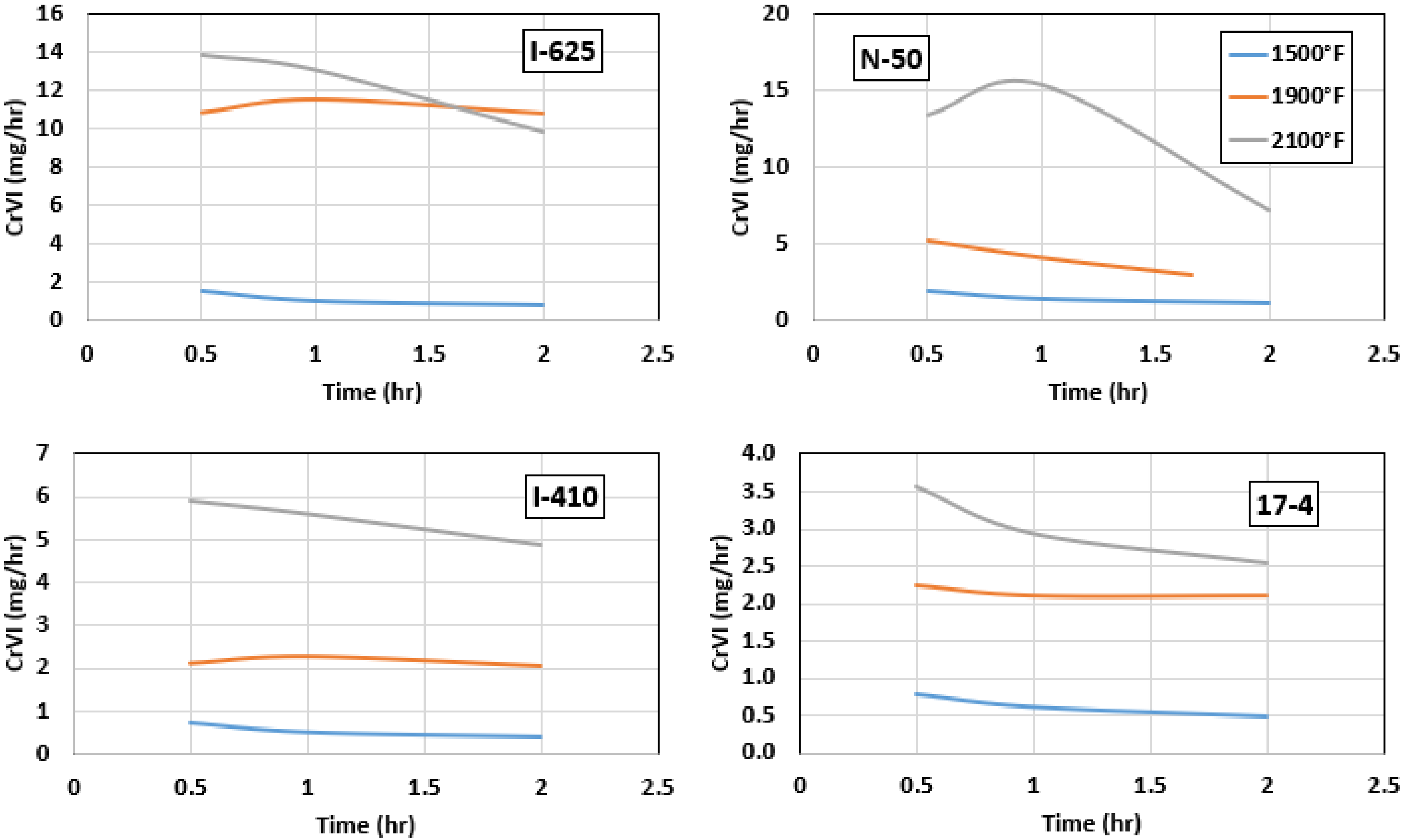
- Hexavalent chromium emissions were detectable starting at 1500°F, with the highest emissions measured at 2100°F
- Samples of the I-625 and N-50 alloys had the largest emission rates regardless of temperature
  - I-625 and N-50 have chromium content ranging from 20.0-23.5%, compared with that of the 410 and 17-4 alloys (12.0-15.5%)
  - The weight and surface area of all the metal alloy specimens were factored into the results

Line graphs on next slide

Results – Metal Alloy Samples
(continued)

Key Takeaways

- Higher furnace temperatures correlated with higher hexavalent chromium emission rates
- Alloys with higher chromium content (I-625 and N-50) emitted higher levels of hexavalent chromium overall



Page 21, Figure 5 – Hexavalent chromium emission results in mg/hr for punchouts

Results – Refractory Material Samples

- Increased furnace temperatures led to increased hexavalent chromium emissions for all refractory materials
- Emission rates were similar for all three refractory material samples
- Chromium content (percent by weight) of refractory material is low compared to other the samples
  - A high percentage of the emissions is suspected to be caused by particles deposited in the furnace from previously charged samples that “seasoned” the furnace hearth bricks and walls

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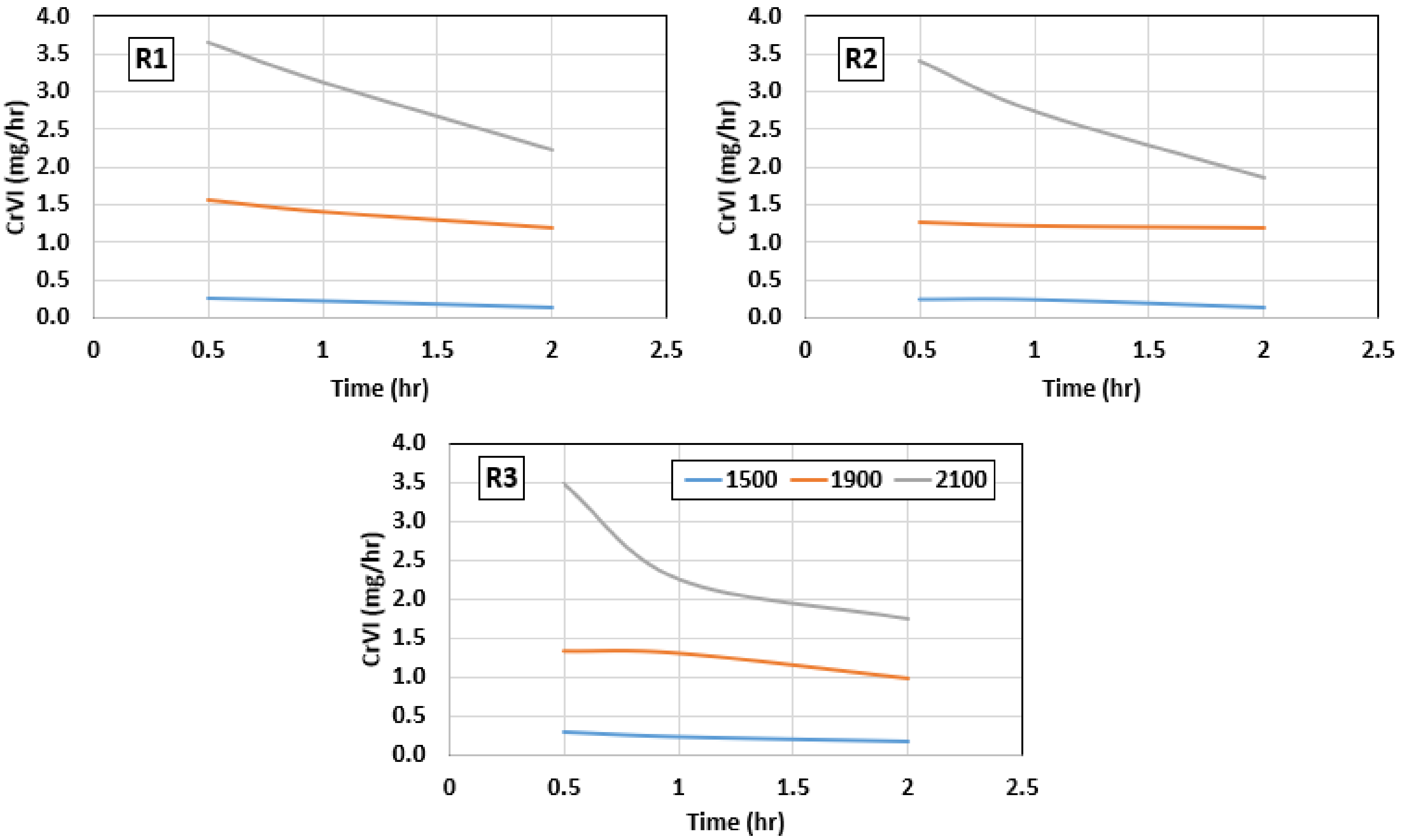
Results – Refractory Material Samples

Key Takeaways

- Higher furnace temperatures correlated with higher hexavalent chromium emission rates
- High percentage of the emissions may be a result of contamination in the furnace



Page 22, Figure 6 – Hexavalent chromium emission results in mg/hr for used refractory material

Results – Racking, Tray, and Needle Samples

- Increased furnace temperatures led to increased hexavalent chromium emissions for all materials
- No measurable hexavalent chromium emissions at 800°F
- Previously used samples and new samples of 304 stainless steel emitted near identical levels of hexavalent chromium when tested at 2100°F
- New HR9 samples emitted nearly double the rate of hexavalent chromium as the used HR9 samples

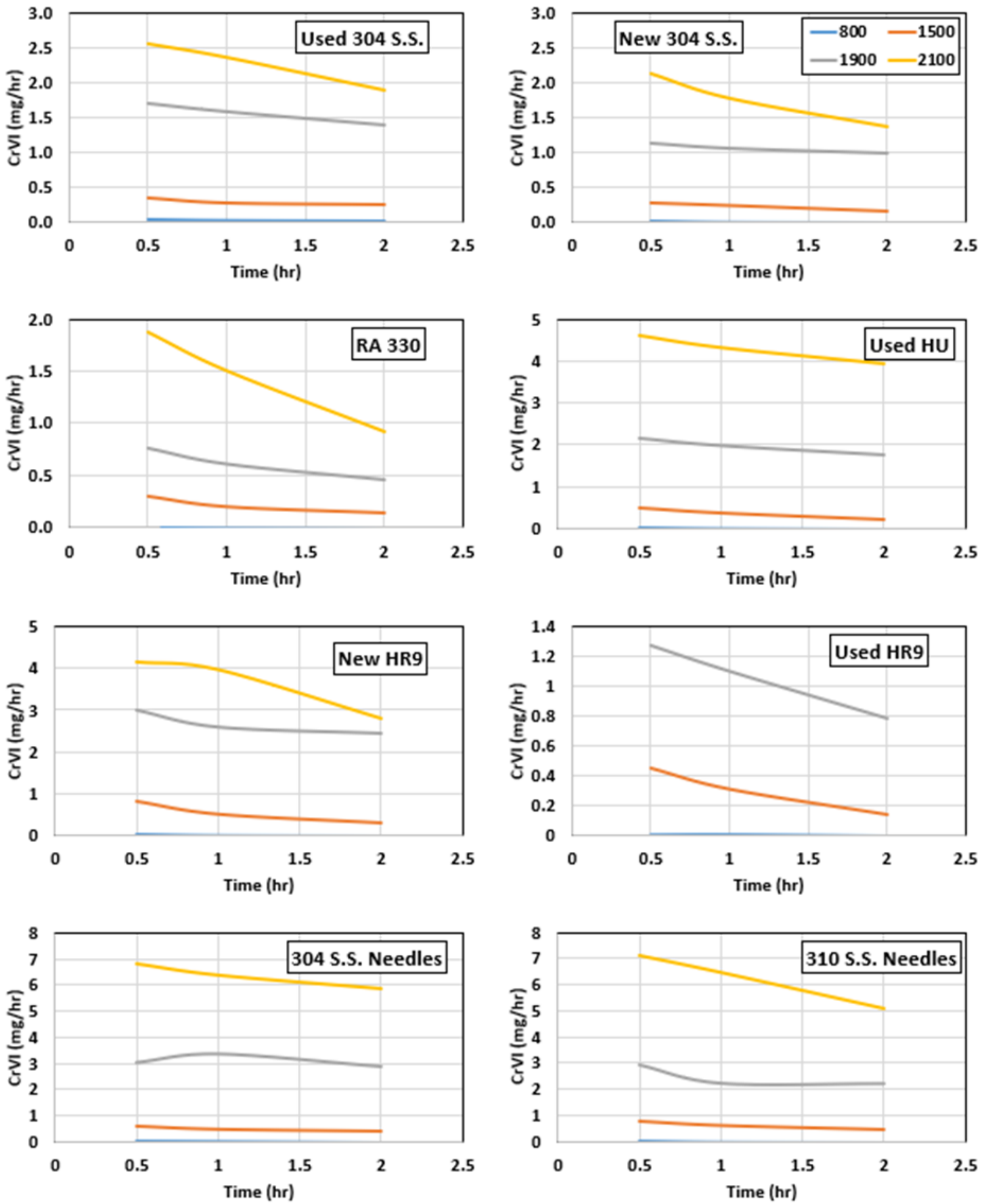
Line graphs on next slide

Results – Racking/Tray/Needle Samples

Key Takeaways

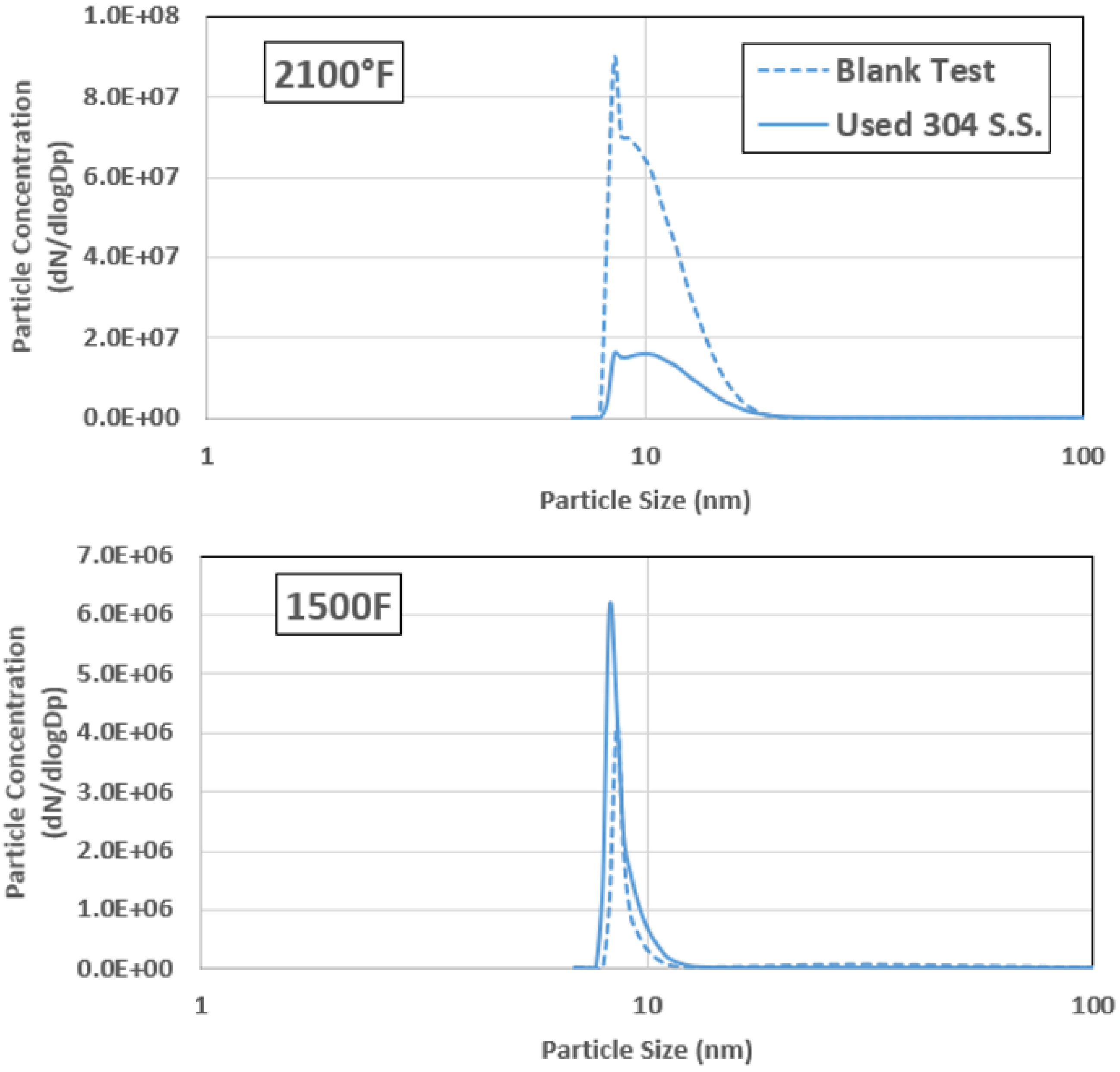
- Higher furnace temperatures correlated with higher hexavalent chromium emission rates
- No measurable hexavalent chromium emissions at 800°F
- Emissions from new and used materials varied depending on the material

Page 24, Figure 7 – Hexavalent chromium emission results in mg/hr for used racking and tray material



Results – Particle Size Distributions

- Particle size distribution was measured during the experiments with the 304 stainless steel and the following blank tests
- For all tests, majority of particles were below 20 nm in diameter
  - Size distribution trends differed between the sample and blank tests during furnace temperatures of 2100°F and 1500°F, respectively
- Small particles in the 10 nm range can penetrate into lower lung airways



Page 28, Figure 11 – Particle size distributions

Results Summary

- CE-CERT study shows that metal heating is a source of hexavalent chromium emissions
- Scale and dust resulting from the metal heating process can contaminate the furnace
- Despite residual emissions from the contamination, trends can be deduced from the data:
  - Lower hexavalent chromium levels after various cleaning procedures showed lower emissions, demonstrating that source of blank emissions is from previous alloy heating
  - Higher chrome content and higher temperatures correlated with higher emissions
  - Emission rates (mg/hr) for all materials decreased over time while in the furnace
- Particle size distribution tests show aerodynamic diameter of all hexavalent chromium emissions from the furnace to be less than 20 nm

Summary of Working Group #2

- South Coast AQMD testing identified hexavalent chromium emission sources:
  - Furnaces
  - Fugitive dust
  - Quench tanks
- Survey results show housekeeping frequency varies widely across industry
  - Regular housekeeping is necessary to minimize fugitive dust buildup
- CE-CERT study results:
  - Hexavalent chromium emissions correlate with furnace temperature and chromium content of samples
  - Contamination from prior furnace use can contribute to hexavalent chromium emissions regardless of material heated

RULE DEVELOPMENT PROCESS

Overview of Rule Development Process

Working group and stakeholder meetings continue throughout process

Information Gathering and Analysis

Preliminary Draft Rule Language and staff report

Released 75 days prior to Public Hearing

Public Workshop

Public comment on Preliminary Draft Rule

Draft Rule Language and Staff Report

Released 30 days prior to Public Hearing

Public Hearing

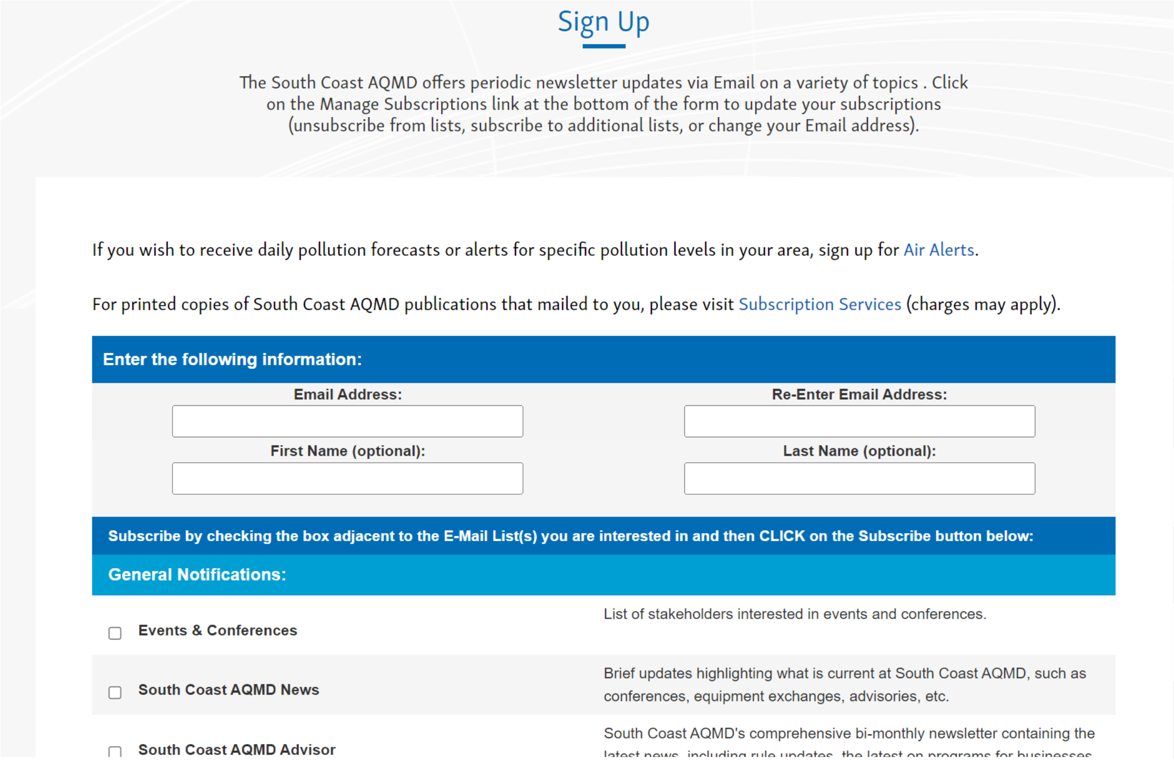
Public comments and Board action

Next Steps

- Continue site visits at facilities
- Develop initial rule concepts
- Working Group Meeting #3
- Public hearing is tentatively scheduled for November 2023

Staying Updated

- Sign up to receive e-mail updates via http://www.aqmd.gov/sign-up



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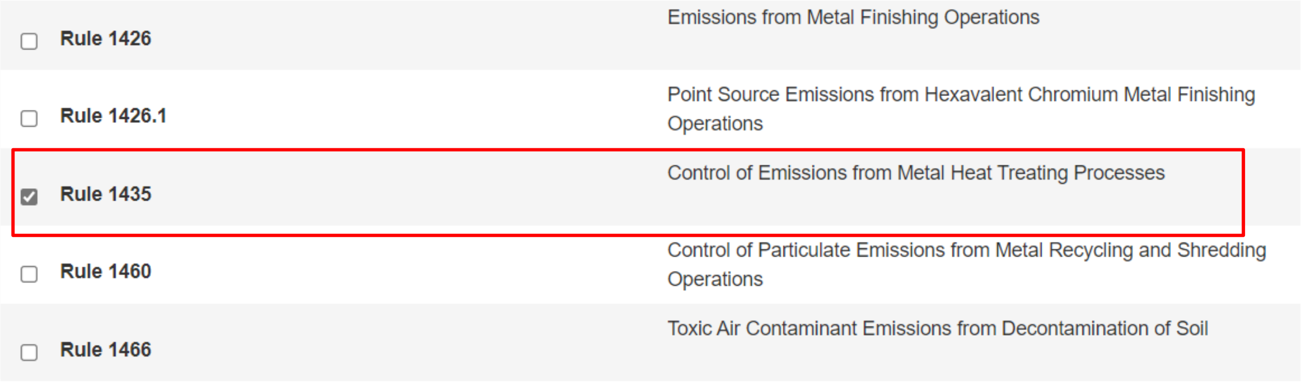

☐ **Rule 1426**	Emissions from Metal Finishing Operations
☐ **Rule 1426.1**	Point Source Emissions from Hexavalent Chromium Metal Finishing Operations
☑ **Rule 1435**	Control of Emissions from Metal Heat Treating Processes
☐ **Rule 1460**	Control of Particulate Emissions from Metal Recycling and Shredding Operations
☐ **Rule 1466**	Toxic Air Contaminant Emissions from Decontamination of Soil

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