

**Final Report**

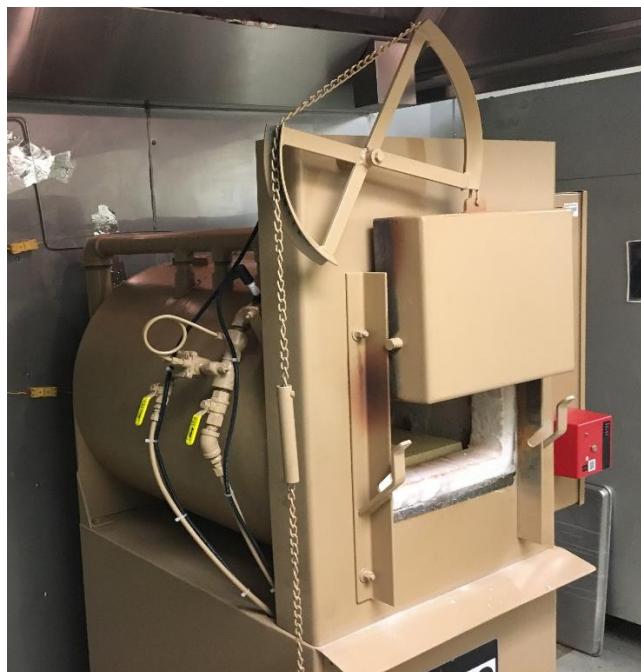
**Hexavalent Chromium Emissions from Industrial Heat-Treating Furnaces**

**Contract #18258**

**Prepared for:**

**South Coast Air Quality Management District  
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**September 2021**



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## **Disclaimer**

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## **Acknowledgments**

This report was prepared at the University of California, Riverside, and Bourns College of Engineering-Center for Environmental Research and Technology (CE-CERT). The authors thank the following organizations and individuals for their valuable contributions to this project.

We acknowledge funding from South Coast Air Quality Management District under contract number 18258. We thank California Metals Coalition and Mr. James Simonelli for their help and guidance during this program.

We dedicate this work to the late Kurt Bumiller.

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## **Executive Summary**

In 2013, the South Coast Air Quality Management District (SCAQMD) responded to community complaints of metallic odors in Paramount, California. Air monitoring in the area by SCAQMD revealed elevated concentration of hexavalent chromium or chromium 6 (Cr6), as well as other toxic pollutants originating from metal forging and heat-treating facilities in Paramount. Although it was found that these facilities are contributors to the rise in ambient level hexavalent chromium, there is a high degree of variability in emissions between these facilities for reasons unknown. SCAQMD identified several mechanisms that may have an effect on the production of hexavalent chromium including, chromium conversion in refractory materials, chromium conversion in stainless steel materials used in furnace construction, conversion in materials being treated, conversion in refractory dust, conversion in supporting racks and trays, conversion in airborne chromium particles, and increased conversion dependent on combustion conditions inside furnace. This study investigated the impact of each process in order to characterize and quantify the mechanisms leading to hexavalent chromium emissions.

For this study, testing was performed on a new high temperature gas heat treat furnace utilizing several different materials including metals, refractory material, and furnace materials that are typical of heat-treating operations in South Coast Air Basin (SCAB). These materials were tested at temperatures of 2100°F, 1900°F, and 1500°F. Rack, tray, and needle materials were tested at 800°F to better understand hexavalent chromium formation at low temperature conditions. Several blank tests were also conducted at all temperature conditions to evaluate the degree of hexavalent chromium contamination in the furnace. Results of this study showed that:

- Hexavalent chromium emissions were detectable starting at 1500°F, with the highest emission rates at 2100°F.
- Hexavalent chromium emissions were strongly depended on temperature, surface area, and chromium content.
- The formation of scale and dust as a result of the heat-treating process can “season” or contaminate the furnace. Thus, high emissions of hexavalent chromium can be produced even from a heated furnace with no processed material.
- Cleaning, extending heating periods with no metals, and furnace coats can be applied to reduce hexavalent chromium emisisions of “seasoned” furnaces.
- Increasing furnace temperatures led to an increase in sub-micron particles, CO<sub>2</sub>, and NO<sub>x</sub> emissions.

## 1. Introduction

In 1986, the California Air Resources Board (CARB) classified hexavalent chromium as a toxic air contaminant. Later in 1990, the U.S. Environmental Protection Agency (USEPA) also identified hexavalent chromium as a toxic air contaminant through the Clean Air Act. Hexavalent chromium (Cr<sub>6</sub>) is a demonstrated human carcinogen according to the International Agency for Research on Cancer (IARC, 2020; Blasiak et al., 2000; Beukes et al., 2017; Bagchi et al., 2007). According to the USEPA, hexavalent chromium is characterized by a cancer potency that is higher than the potency of the other regulated heavy metals by 2-3 orders of magnitude (USEPA, 2019). If combined with potassium or sodium in form of chromates, hexavalent chromium is readily soluble in water (IARC, 2020). This behavior, coupled with hexavalent chromium toxicity, makes this compound a serious contaminant of groundwater in the vicinity of hexavalent chromium sources (Tiwari et al., 2019). Inhalation of hexavalent chromium has shown a clear cause-effect relationship with the development of lung, sinus and nasal cancer (IARC, 2012). Contrary to trivalent chromium (Cr<sub>3</sub>), hexavalent chromium is able to penetrate the cell membrane. Hexavalent chromium is unreactive to DNA but the intracellular reduction of Cr<sub>6</sub> may produce high levels of Cr<sub>3</sub>, which is the agent responsible for DNA damage (Sun et al., 2015).

Chromium is a naturally occurring metal found in Earth's Crust that is commonly used in many alloys for its beneficial properties including resistance to impact, corrosion, and oxidation (Barceloux et al., 1999). The main uses of chromium include metallurgical (67%), refractories (18%), and chemical (15%) (Saha et al., 2011). Chromium at a naturally occurring oxidative state of chromium (III) is a necessary element in both humans and mammals. However, at higher temperatures trivalent chromium can reach an excited state and oxidize into the higher-valent hexavalent chromium (Barceloux et al., 1999). Chromium has a number of industrial applications

as it is used in paints and pigments, in metal plating, in the leather tanning industry, in the steel industry, as wood preservative, and as catalyst (Vaiopoulou and Gikas, 2020).

The oxidation of trivalent chromium to hexavalent chromium is a complicated process that is not clearly understood and is dependent on several factors including composition, humidity, temperature, and other meteorological factors (Yu et al., 2014, Swietlik et al., 2010). Both trivalent chromium and hexavalent chromium can be found in many different species depending on availability of oxygen and other alkali earth metals (Sokolov, 2011, Chen et al., 1997). This makes the oxidation process of trivalent chromium to hexavalent chromium very difficult to quantify as each species will form at different temperatures and conditions. The thermal behavior of some species has been studied by researchers, however the transformation temperature, and chemical composition of products have not been recorded in relation to the research procedure used (Sokolov, 2011). It is therefore of great importance to investigate the effects of hexavalent chromium emissions for every material.

Although it is known that elevated temperatures are necessary for trivalent chromium to oxidize into hexavalent chromium, the temperature at which this occurs changes depending on the input material (Mao et al., 2015, Nath et al., 2018, Wu et al., 2019). Some studies have shown that oxidation of trivalent chromium to hexavalent chromium can start to occur around 800°F, while others state the oxidation process begins around 1000°F (Chen et al., 1997, Nath et al., 2018). Although elevated temperatures do increase the amount of oxidation to hexavalent chromium, increasing the temperatures above a threshold, depending on the material composition, will cause the hexavalent chromium to revert back to trivalent chromium. This temperature can vary and is shown to be around 1500°F for the hexavalent chromium species of  $\text{CrO}_3$  to revert to the trivalent chromium species of  $\text{Cr}_2\text{O}_3$  (Sokolov, 2011), while another study showed this to be around 2700°F

for the hexavalent chromium species  $\text{Ca}_4\text{Al}_6\text{CrO}_{16}$  to reduce to the trivalent species of  $(\text{AlCr})_2\text{O}_3$  (Nath et al., 2018).

In some cases, however, the material composition is more important to hexavalent chromium production than temperature (Wu et al., 2019). It has been shown that the presence of metals can inhibit or help oxidize hexavalent chromium. For example, sulfur and sodium inhibits the oxidation to hexavalent chromium while Chlorine helps oxidize hexavalent chromium (Chen et al., 1997). During the heat-treating process it is expected that the material structure of the metals will change depending on the temperatures and heating times. Although there may be a change in material structure the initial valence of chromium has no effect on the relative ratio of hexavalent chromium to total chromium in the emissions (Linak et al., 1995).

Although hexavalent chromium oxidation has been studied, the knowledge of its emissions from heat treating furnaces is extremely sparse and almost no literature exists concerning this issue. Huang et al. (2014) characterized the total and soluble hexavalent chromium concentrations in ambient PM in New Jersey during wintertime and summertime. They found that the summer mean ratios of soluble to total hexavalent chromium were significantly higher than in the winter, and the winter concentrations of soluble hexavalent chromium in the suburban area were significantly lower than in the urban areas. The results suggested that formation of hexavalent chromium via atmospheric chemistry may contribute to the higher soluble hexavalent chromium concentrations in the summer. A different study also showed that higher hexavalent chromium concentrations may be attributed from photooxidation reactions of trivalent chromium to hexavalent chromium in the summer, as well as an enrichment of hexavalent chromium in PM<sub>2.5</sub> emissions (Yu et al., 2014). Much of the publicly available information on hexavalent chromium formation and emissions are based on studies from processes such as welding, refractory production, and



smelting, as opposed to metal heat treating. This program was designed to mimic industrial scale processes of metal heat treating in laboratory conditions for the better understanding of hexavalent chromium emissions from typical materials processed in facilities in the South Coast Air Basin (SCAB).

## 2. Experimental Procedures

### 2.1 Test Protocol

For this project, testing was performed using materials provided by the California Metals Coalition (CMC) and their member companies operating facilities in SCAB. Test specimens included metals, refractory material, and furnace materials that are typical of heat-treating furnace operation in SCAB. Table 1 lists all test specimens used for this project, including 4 different alloys from punch-outs, 3 used refractory materials, and 8 more specimens such as needles, racks, and tray metals.

**Table 1. Test materials**

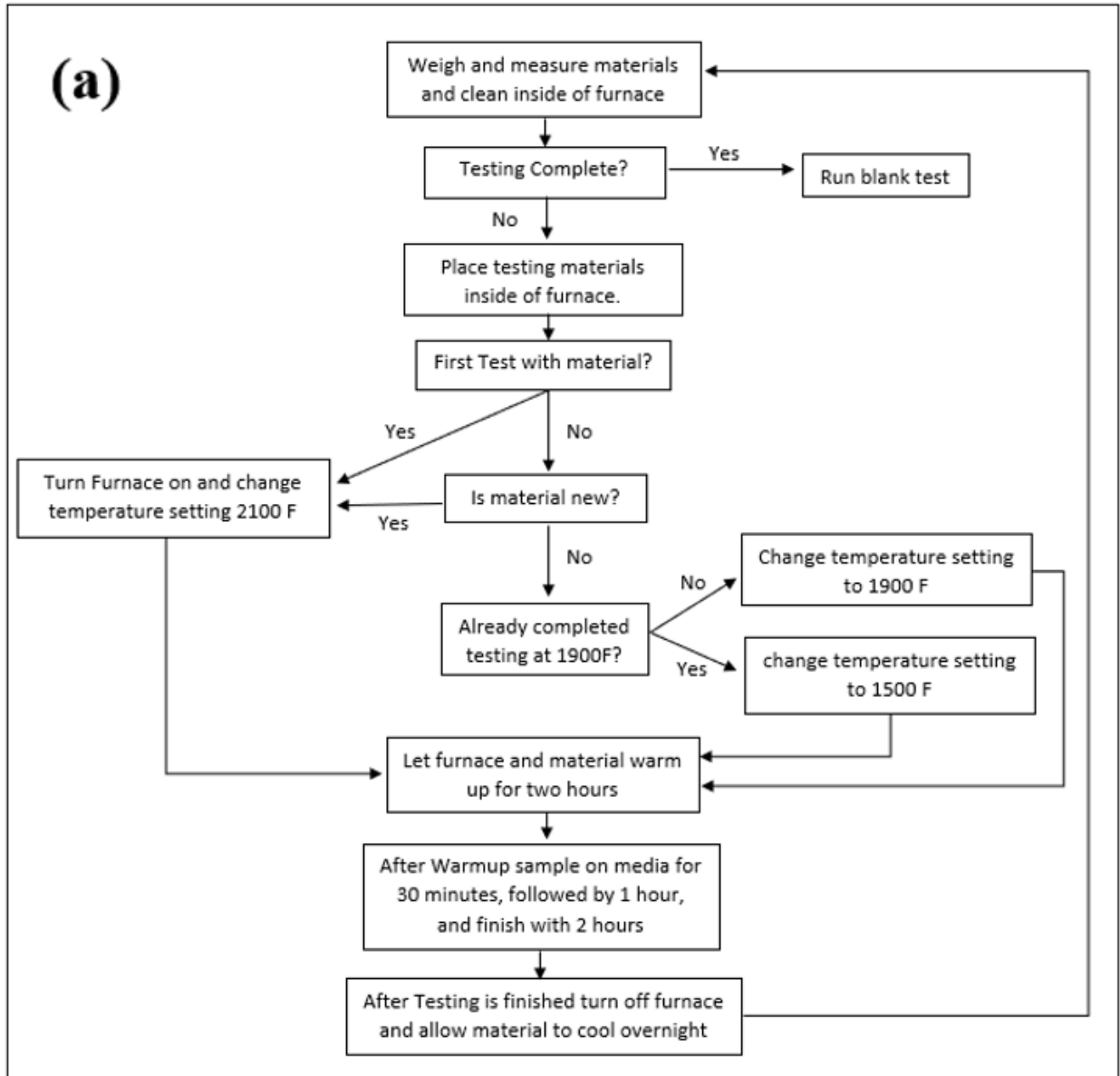
<b>Punch Outs</b>	
Material	Quantity
I-625	5
410	5
N-50	5
17-4	5
<b>Refractory</b>	
Material	Quantity
1	4
2	4
3	4
<b>Racking/tray/needles</b>	
Material	Quantity
310 S.S. Needles	0.905 lbs.
304 S.S. Needles	1.015 lbs.
304 SS Racking Material (used)	1
304 SS Racking Material (new)	1
HR9 racking Material (used)	1
HR9 racking material (new)	1
HU (used)	2
RA330 (used)	2

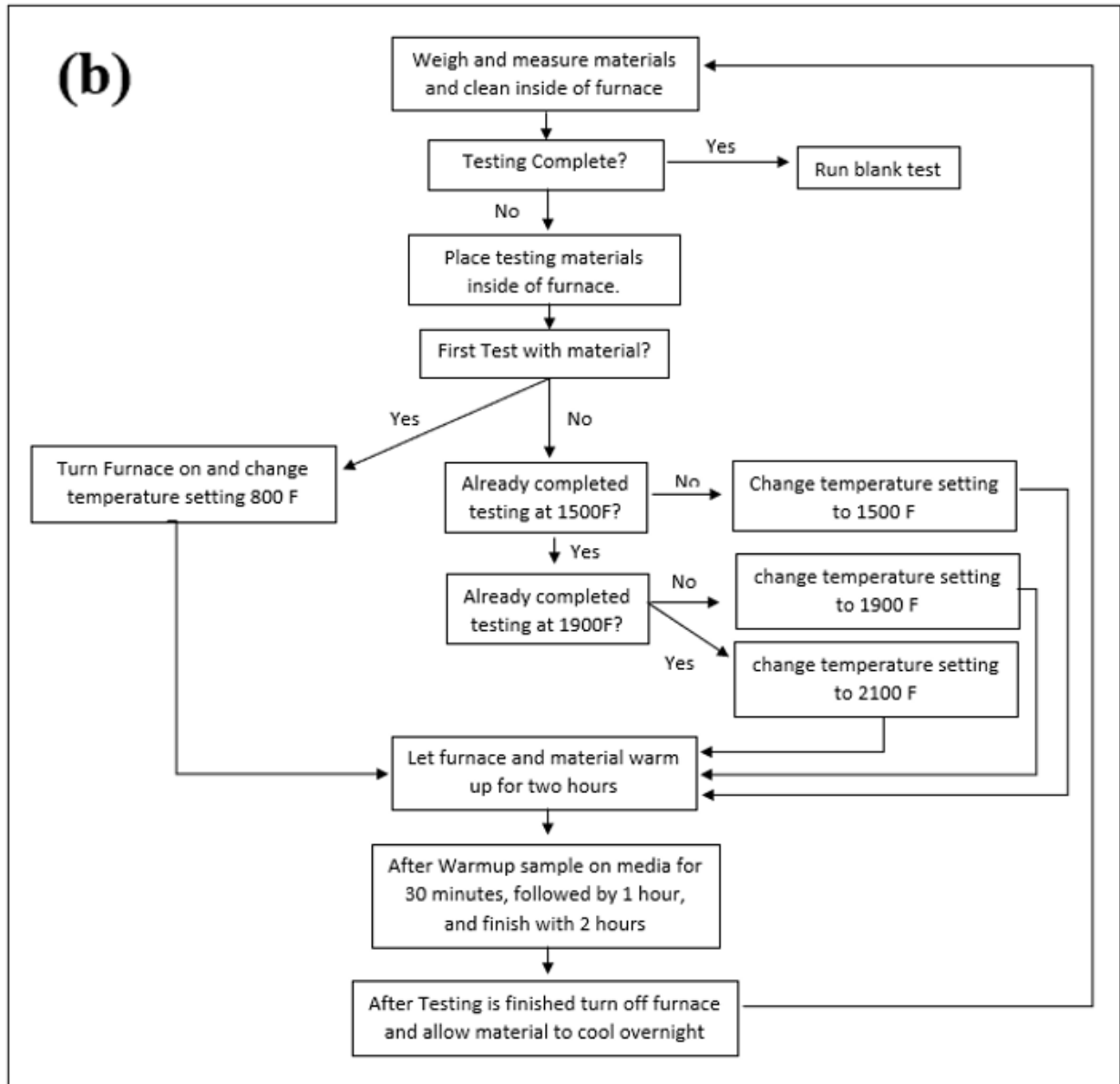
Each material was tested at 3 or 4 different temperatures followed by a blank test. The furnace was cleaned every day prior to testing. Testing started with the punchouts and refractory material as these are the types of materials to be considered as elevated hexavalent chromium sources in for the heat-treating industry. The metal alloy punchouts were tested 5 at a time in the furnace, and the refractory material were tested 4 at a time to ensure there is enough hexavalent chromium emissions for each sample. For the metal punchouts, data sheets were provided by CMC that show the nominal composition for these 4 different alloys. Additional information including chemical composition for each alloy can be found in Appendix A. It is important to note that the refractory material to be tested will contain some chromium, although newer refractories do not use chromium and much of the industry uses the newer form of refractories during their operations. Stainless steel needles, used to help keep door jambs and refractory material together, as well as different racking material and tray material typical to industry were also tested after the punchouts and refractory material.

Testing on each material was performed at temperatures of 2100°F, 1900°F, and 1500°F. Rack, tray, and needle materials were tested at 800°F to better understand hexavalent chromium formation at low temperature conditions. These temperatures were chosen as being representative of typical heat-treating processes of different metals used in the industry. The range of testing temperatures will provide a broad understanding of the hexavalent chromium emissions of heat-treating cycles used in the industry. Testing was performed from highest temperature to lowest temperature for the punchouts and refractory materials. Testing from the lowest temperature to the highest temperature was performed on the rack, tray, and needles due to the potential drastic changes in the material structure of the specimens at high temperatures.

Prior to testing, all metal specimens were weighed and measured for height and diameter in order to calculate an approximate surface area. Before introducing the metal specimen into the furnace, the interior of the furnace was cleaned by vacuuming residual particles and dust to prevent sample contamination. The furnace was characterized by performing blank tests (with no specimens) to show hexavalent chromium emissions were negligible.

Initial testing showed that relatively short sampling times of 30 minutes, 1 hour, and 2 hours would provide the optimum results in terms of hexavalent chromium concentrations and temperature at the duct. Sampling started after a two-hour warm-up at each testing temperature to ensure the material was fully and uniformly heated. Figure 1(a-b) describes the testing protocol for the materials of this study.





**Figure 1(a-b): (a) Testing protocol for punchouts and refractory bricks and (b) Testing protocol for tray and racking materials**

## 2.2 Furnace and Analytical Methods

For the purpose of this program, a new furnace was purchased to perform the experimental work (Figure 2). The furnace was a high temperature gas heat treat furnace, model HTG-98 and manufactured by McEnglevan Industrial Furnace Company (MIFCO). The furnace used automatic temperature control and proportioning burner systems with standing pilot, spark ignition and

ultraviolet safety systems. The furnace was natural gas fired in which eight burners were staggered along the chamber walls utilizing a tangential method of firing for the development of a swirling sheet of flame that hugged the chamber walls and heated the chamber uniformly. The temperature range of the furnace was 400°F - 2200°F, which meets the temperature ranges of typical industrial heat-treating processes. The gas input of the furnace was 350,000 BTU/hr and the chamber dimensions were 15W-13H-25D. Table 2 lists the main technical specifications of the furnace. The furnace was designed to contain no chromium in the refractory insulation or hearth bricks that will lead to hexavalent chromium formation.



**Figure 2. Furnace setup**

**Table 2. MIFCO HTG-98 specifications**

<b>Furnace Model</b>	HTG-98
<b>Door Size</b>	12''w x 8''h
<b>Chamber Size</b>	15''w x 13''h x 25d''
<b>Hearth Size</b>	11''w x 24½''l
<b>Gas Input (BTU/hr)</b>	350,000
<b>Motor Rate</b>	½ Hp 3600 rpm
<b>Blower Rate</b>	90 cfm

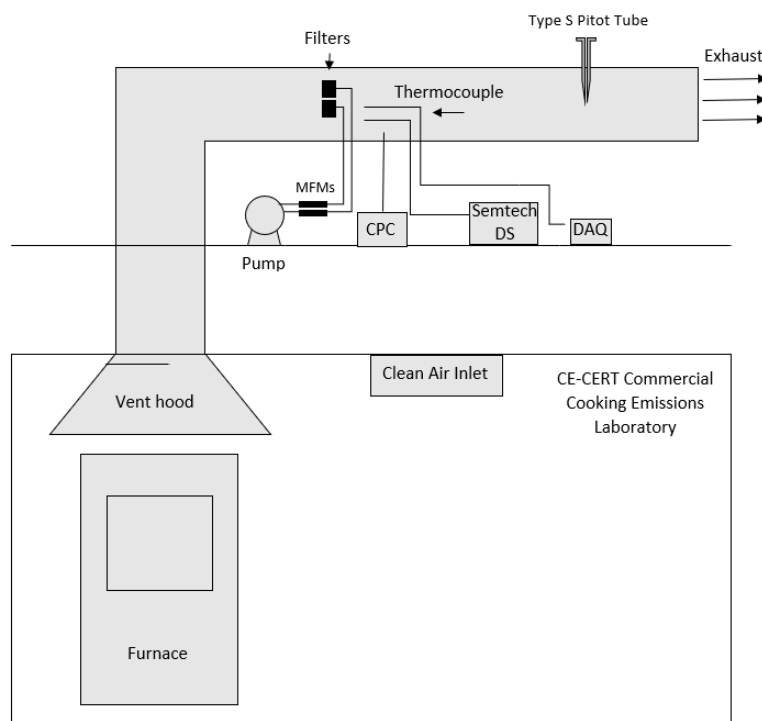
<b>O.A. HT.</b>	72"
<b>Floor Space</b>	42x42
<b>Gas Connection</b>	1"
<b>Gas Service</b>	1½ "
<b>Approximate Weight</b>	1560 lbs

A sample of the exhaust gas from the furnace was collected on a sodium bicarbonate impregnated cellulose filter and a 47 mm Teflon filter, respectively, approximately 21 feet downstream of the furnace outlet and 11 feet downstream of a 90-degree bend in the duct. A schematic of the sampling system and setup is shown in Figure 3. Filter holders were placed inside the duct facing the exhaust stream. Due to the relatively high velocity of air through the duct, testing was performed non-isokinetically. The sodium bicarbonate (NaHCO<sub>3</sub>) impregnated ashless cellulose filters were prepared and provided by SCAQMD. The filters were kept in below freezing temperatures when stored at CE-CERT until just before sampling to prevent any decomposition of the solution. The Teflon filters were prepared and provided by CE-CERT. An active open face filter collection method was utilized pulling exhaust gas through the filter face at a rate of 12-15 lpm. The filter flow was controlled using an orifice and measured using a Sierra Mass Flow Meter (MFM). The filters were grouped and shipped to SCAQMD analytical laboratory for analysis every two weeks. The bicarbonate cellulose filters were analyzed by SCAQMD using ion chromatography (IC) in order to obtain hexavalent chromium concentrations. A subset of the Teflon filters was analyzed using X-Ray Fluorescence (XRF) for total chromium emissions, as well as for other metals and elements.

For the determination of hexavalent chromium, the filters were extracted by sonicating in 20 mM sodium bicarbonate solution for one hour. The extract was filtered, then analyzed by ion chromatography consisting of a system comprised of a guard column, analytical column, a post-



column derivatization module, and a UV-Vis detector. During the analysis procedure, hexavalent chromium exists as chromate due to the near neutral or basic pH of the eluent. After separation through the column, hexavalent chromium forms a complex with diphenylcarbazide (DPC) forming a chromophore which is detected at a wavelength of 530 nm. The resulting hexavalent chromium chromatographic peak retention time and height/area were determined using the Dionex Chromeleon® software. This method is based on a modification of the California Air Resources Board method (Hexavalent Chromium in Ambient Air Method CARB MLD-039 (<https://www.arb.ca.gov/aaqm/sop/mld039.pdf>)).



**Figure 3. Schematic of the sampling system**

The furnace was positioned underneath an exhaust hood inside of CE-CERTs Commercial Cooking Emissions laboratory. The exhaust hood extended over the entire furnace to ensure that the total exhaust will be swept into the duct. The exhaust gasses were mixed with ambient air

through a 16 inch inner diameter duct. Duct flow was set using a variable speed drive and was set in such manner to ensure that the dilution ratio did not exceed 100:1 and the temperature inside the duct was kept below 140°F to prevent evaporation of the sample. A TSI 3022A condensation particle counter (CPC) and Semtech DS gas analyzer were also utilized downstream of the filter to measure particle number (PN), as well as carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitrous oxide (NO), and total hydrocarbons (THC). Temperature measurements were made inside the furnace, just before the duct inlet and at the sample filter location. Both temperature and filter flow were monitored and recorded using a Measurement Computing Data Acquisition System (DAQ).

Duct pressure measurements were made using a type S pitot tube to meet EPA protocol method 2 standards in order to calculate duct flow. The pitot tube was placed inside the duct, 16 feet after a 90-degree bend, 5 feet after the filters, and was secured in the middle of the duct. Pressure measurements were performed periodically throughout the test day using a Dwyer Series 475 digital manometer. Using EPA protocol method 2, duct flow measurements were calculated to obtain the hexavalent chromium emissions on a mass emission rate (mg/hr). Dilution ratio was calculated at each temperature prior to testing by measuring the ambient air concentration, raw concentration, and duct concentration of CO<sub>2</sub> and NO<sub>x</sub>. Pictures of the Commercial Cooking Emissions Laboratory and sampling system are shown in Appendix B.

### **3. Results**

#### **3.1 Blank Tests**

Blank tests were conducted at 1500°F, 1900°F, and 2100°F prior to firing any metal inside the furnace. Blank tests were also conducted at 2100°F in between different material tests. Figure 4 shows the emission rates of every blank test that was conducted at 2100°F. Initial emission rates of hexavalent chromium were extremely low, however, as loaded tests were performed the furnace blank emission rates increased dramatically. It is theorized that as different materials were tested, a dust was formed around the furnace comprised of material particles absorbed in the porous furnace walls and hearth bricks. These particles rich in hexavalent chromium were accumulated in the furnace surfaces and released at a later time during high temperature testing. Many of the metals tested produced scale at higher temperatures leading to more dust being formed.

Several different approaches were performed in between tests to remove the dust from the furnace walls and to lower the emission rates for the blank tests. These approaches included hand cleaning hearth bricks and furnace walls with a wire brush and vacuum, heating the furnace at 2100°F for extended amount of time to burn out excess chromium, cleaning hearth bricks and furnace walls with a wire drill bit and vacuum, and applying a furnace coat over hearth bricks and walls. All different approaches were proved to reduce emissions of hexavalent chromium compared to previous tests, with extensive cleaning showing greater reductions in hexavalent chromium emissions.

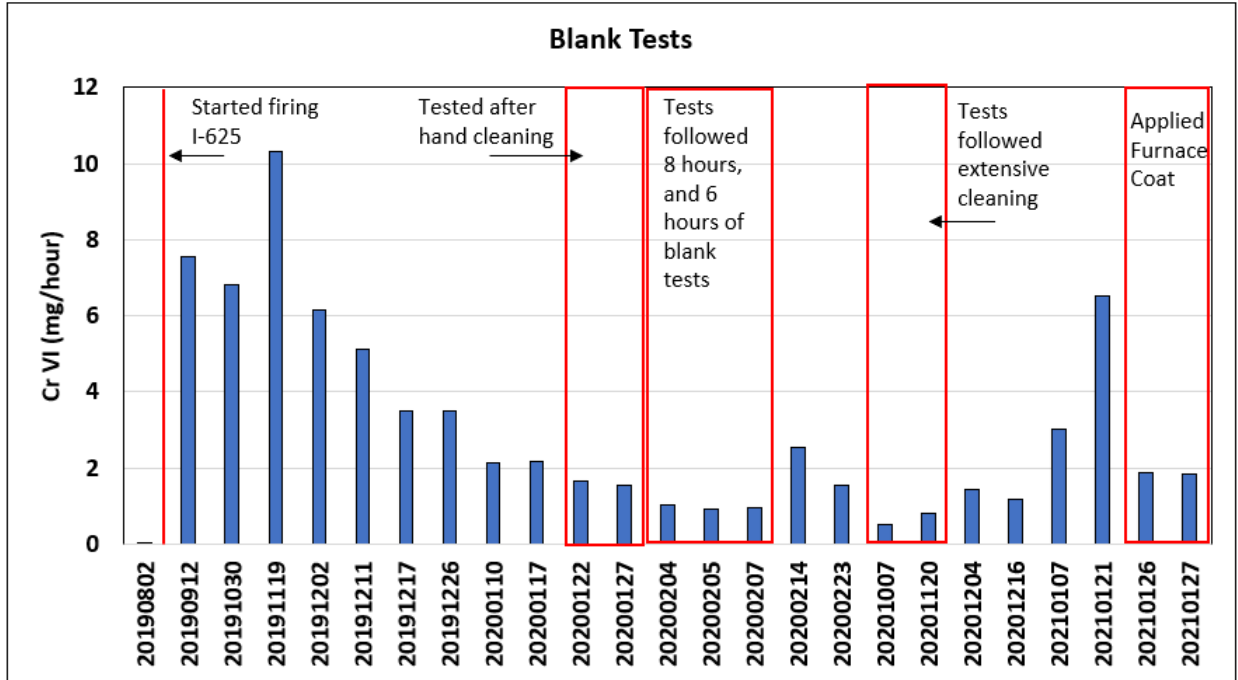


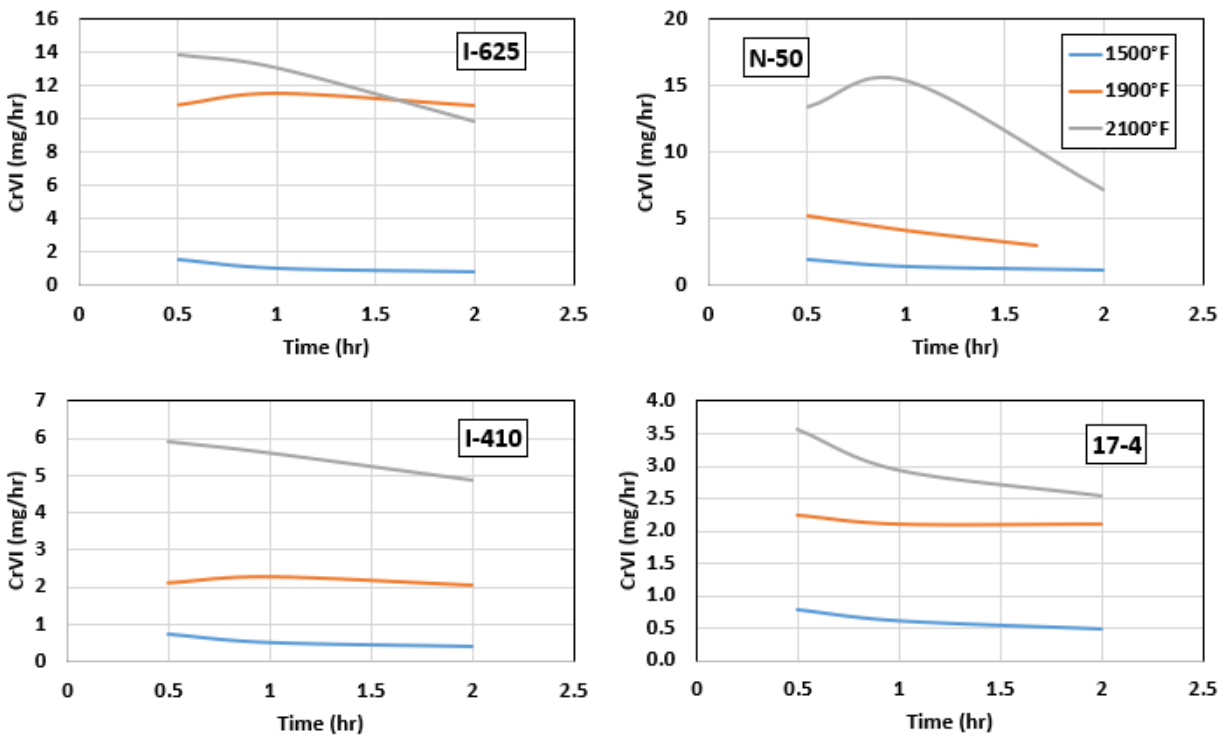
Figure 4. Hexavalent chromium emissions obtained from blank experiments

### 3.2 Punch-Outs

Hexavalent chromium emissions, expressed in mg/hr, for the punchout metal samples are shown in Figure 5. The punchout metals were chosen as typical metals used in heat-treating facilities located in SCAB. Increased furnace temperatures typically led to the increase formation of hexavalent chromium emissions, regardless of metal composition. While there are no similar studies available in the open literature, an earlier work showed decreased amounts of hexavalent chromium present in particles with decreasing flame temperature from a laboratory flame (Werner et al., 2006). The samples of I-625 and N-50 exhibited the highest emission rates of hexavalent chromium of all punchouts regardless of the temperature conditions. Emission rates for the I-625 and N-50 samples ranged from 0.8 mg/hr to 15.3 mg/hr, while I-410 and 17-4 samples ranged from 0.4 mg/hr to 5.9 mg/hr. The samples of I-625 and N-50 also contained the highest chromium

content (20-23%), while I-410 and 17-4 samples had much lower chromium concentrations (12-15%).

The surface area of the punchouts varied based on the actual geometry sample size. It should be noted that the I-410 and 17-4 punchouts were smaller in size than the I-625 and N-50 punchouts, with 37% and 60% less surface area, respectively. When factoring the sample's surface area, N-50 showed the highest hexavalent chromium emission rates at 2100°F (0.0078 mg/hr\*cm<sup>3</sup>), followed by I-625 (0.0075 mg/hr\*cm<sup>3</sup>). The samples of I-410 and 17-4 still showed the lowest emission rates when factoring the sample's surface area, with hexavalent chromium emissions being 32% and 40% lower compared to N-50, respectively.

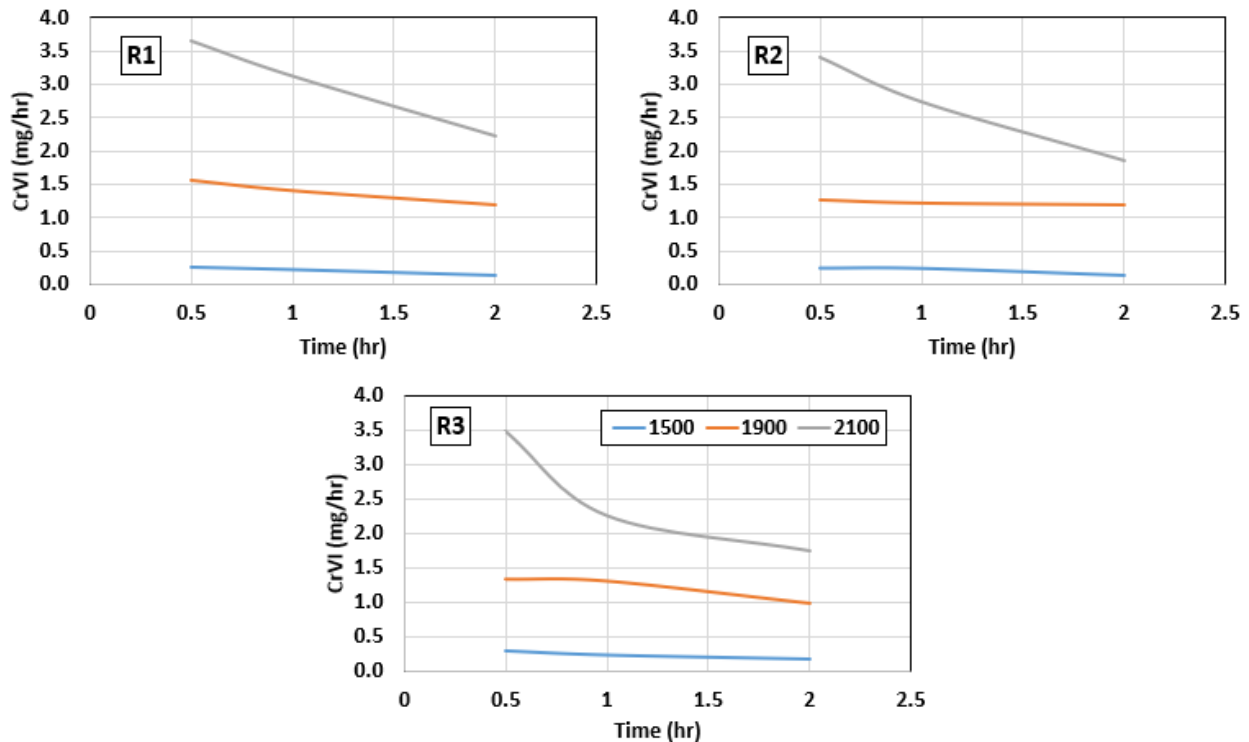


**Figure 5. Hexavalent chromium emission results in mg/hr for punchouts**

### 3.3 Refractory

Hexavalent chromium emissions for the used refractory material are shown in Figure 6. Results showed that higher furnace temperatures led to elevated overall hexavalent chromium

emissions for all refractory materials. The emissions rates remained consistent for each refractory material that was tested. Emission rates for each material tested ranged from 0.1 mg/hr to 3.7 mg/hr. The R1 sample had an average chromium content of 0.52 wt%, while R2 and R3 samples had average chromium contents of 0.16 wt% and 0.25 wt%, respectively. It is important to note that furnace blanks at 2100°F showed similar hexavalent chromium emissions rates to loaded tests with furnace bricks. Initial hand cleaning of hearth bricks and furnace walls was performed after finishing testing on the refractory materials. It is possible that a high percentage of the emission rates were caused by “seasoned” furnace hearth bricks and walls.



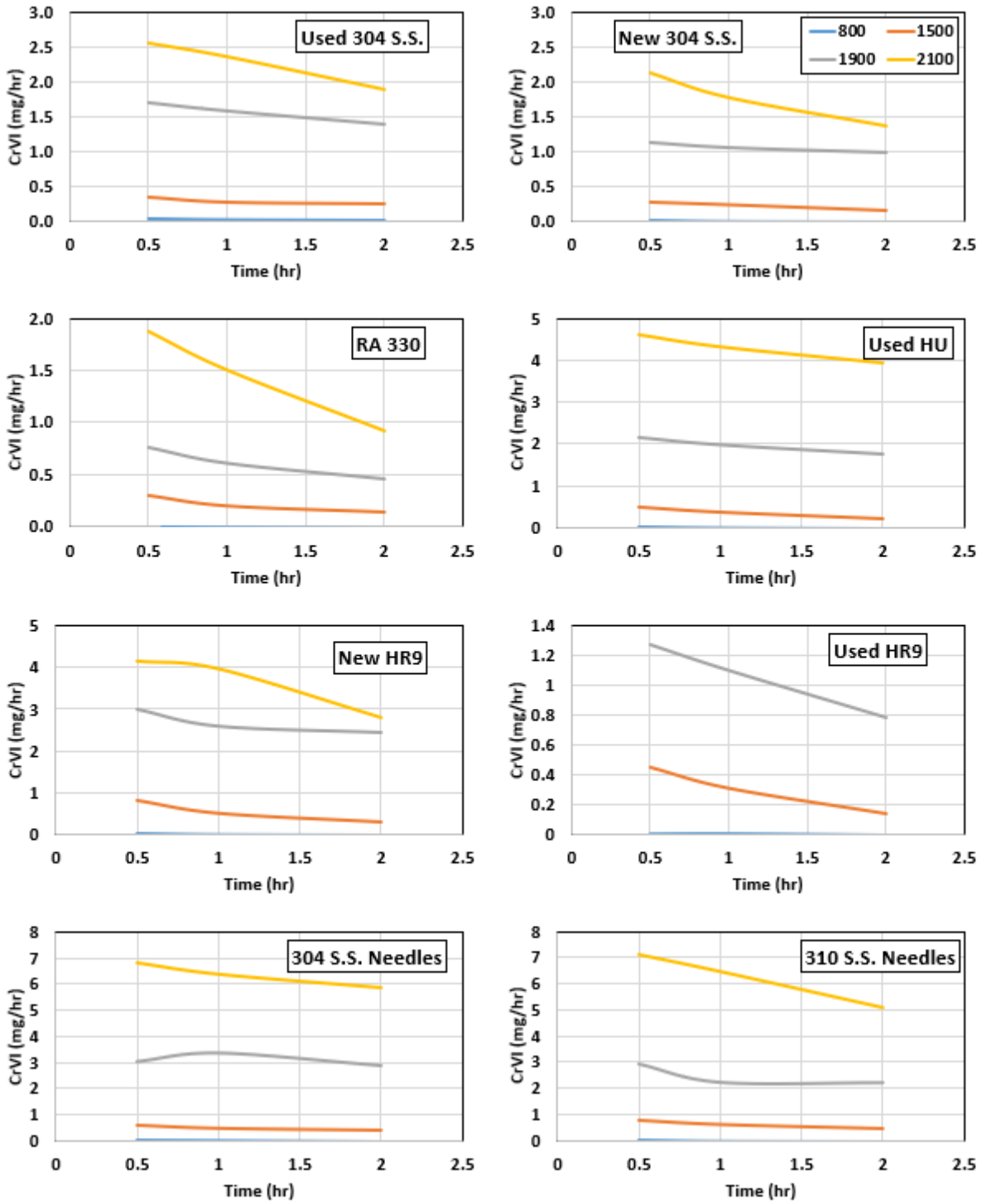
**Figure 6. Hexavalent chromium emission results in mg/hr for used refractory material**

### 3.4 Racking/Tray/Needles

Hexavalent chromium emissions for the racking, tray, and needles materials are shown in Figure 7. Similar to punchouts and refractory materials, increased furnace temperatures resulted to increased hexavalent chromium emission rates. No material showed measureable hexavalent

chromium emissions at 800°F, suggesting that at these temperature conditions little or no hexavalent chromium is expected to be formed. Hexavalent chromium emissions rates ranged from 0.1 mg/hr to 0.8 mg/hr for all materials at 1500°F. Emissions rates ranged from 0.9 mg/hr to 7.1 mg/hr for all materials at 2100°F. The samples of 304 stainless steel needles and 310 stainless steel needles showed the highest hexavalent chromium emission rates of any rack/tray material.

New and used materials were compared to better understand how potential changes in their structure (i.e., surface area) can affect hexavalent chromium emission rates when heat-treated. Samples of used 304 S.S. and new 304 S.S. emitted hexavalent chromium at near identical levels when tested at a furnace temperature of 2100°F (0.0067 and 0.0061 mg/hr\*cm<sup>3</sup>). Due to the irregular shape of the new and used HR9 samples hexavalent chromium emission rates were compared as a function of their weight instead of their surface area. When factoring in the total sample weight, new HR9 sample showed almost double hexavalent chromium emission rates compared to the used HR9 sample, with values of 0.27 mg/hr\*lb and 0.13 mg/hr\*lb.

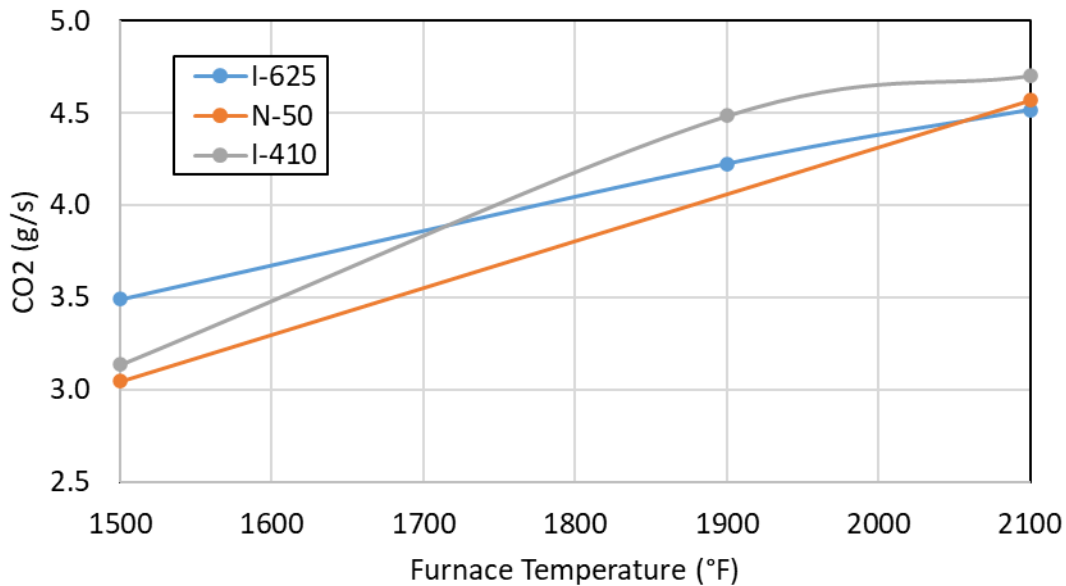


**Figure 7. Hexavalent chromium emission results in mg/hr for used racking and tray material**

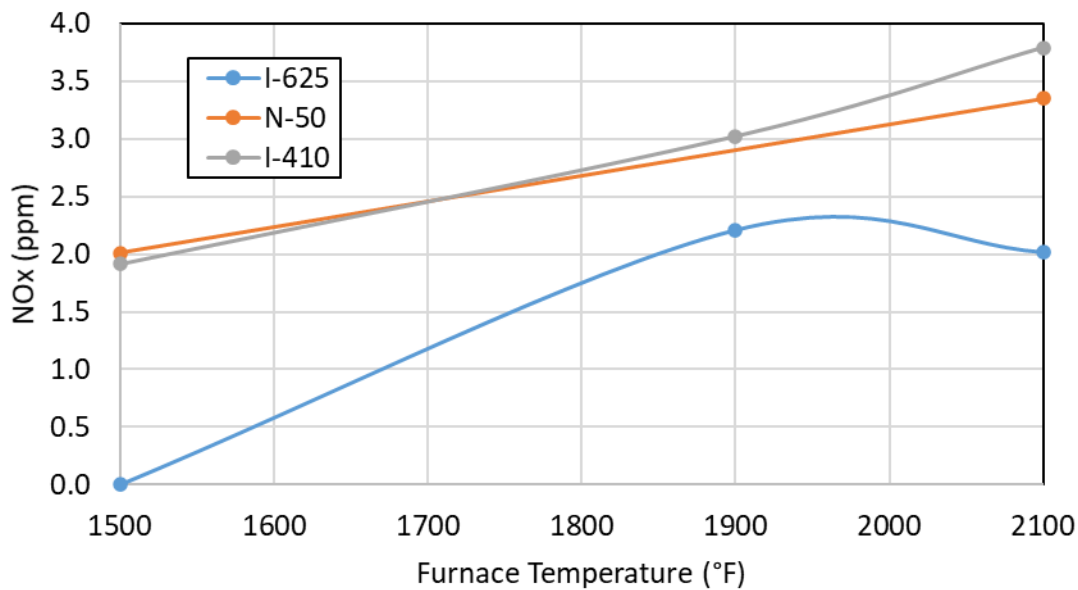


### 3.5 CO<sub>2</sub> and NO<sub>x</sub> emissions

CO<sub>2</sub> emissions in the furnace ranged from 3.0 to 4.7 g/s when the punchouts were tested (Figure 8). In all cases, increasing furnace temperature led to an increase in CO<sub>2</sub> emissions. CO<sub>2</sub> production is directly correlated with the amount of fuel used (i.e., for this study was natural gas). Longer periods of 100% power are needed in order to increase furnace temperature. Figure 9 shows NO<sub>x</sub> emissions as a function of furnace temperature. As temperatures increase NO<sub>x</sub> emissions typically increase as well. However, the production of NO<sub>x</sub> is extremely low with concentrations below 4ppm inside of the duct.



**Figure 8. CO<sub>2</sub> emissions as a function of furnace temperature**

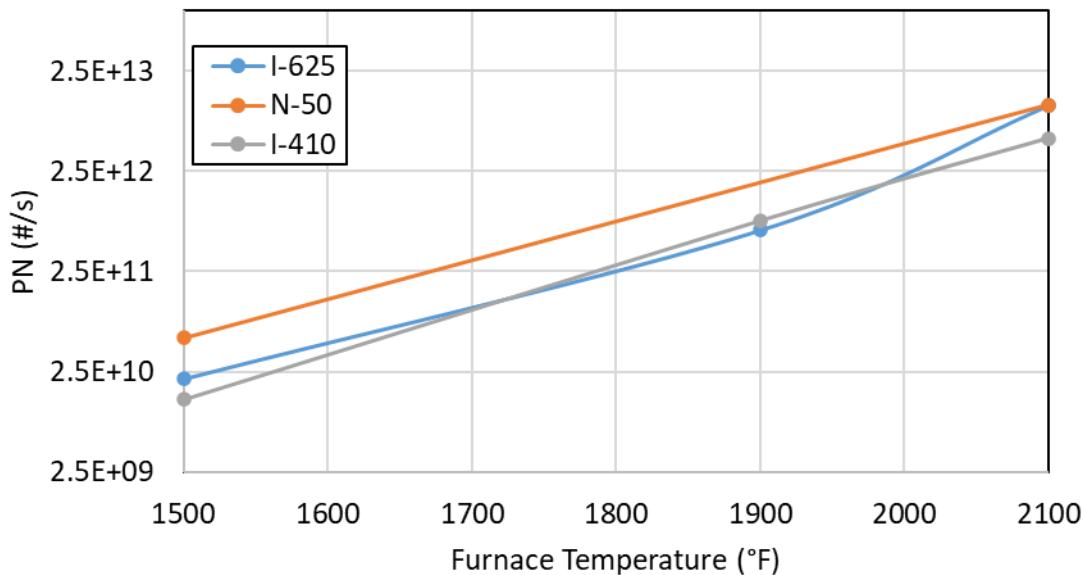


**Figure 9: NOx emissions as function of furnace temperature**

### 3.6 Particle Number emissions

Particle number emissions were measured with an ultrafine 3776 TSI, Inc. condensation particle counter (CPC) with a 2.5 nm cut point. The instrument operated at a flowrate of 1.5 L/min. As shown in Figure 10, particle number emissions increased with increasing temperatures in the furnace. This result agrees with the elevated hexavalent chromium emissions at higher temperatures when a variety of different samples were tested in the furnace. This finding indicates that at higher heat-treating temperatures more ultrafine particles rich in hexavalent chromium are formed. It is known that ultrafine particles can have relatively long atmospheric lifetimes (1-10 days for particles between 10-100 nm) and they can also be transported over long distances. These particles can also undergo extensive atmospheric transformations, such as the formation of secondary aerosols through photochemical reactions and the new formation of hexavalent chromium in ambient air (Werner et al., 2006; Yu et al., 2014; Nico et al., 2009). However, it has been reported that hexavalent chromium in ambient aerosol can be generally decreased over time,

suggesting that the toxicity associated with hexavalent chromium particle will also be decreased over time (Werner et al., 2006). This is an important finding in terms of workplace exposure to hexavalent chromium emissions, as well as to exposures in nearby communities from heat-treating facilities. It should be noted that even if hexavalent chromium reduced to trivalent chromium on a relatively long timescale in the atmosphere, there can still be significant exposure for populations that are near the hexavalent chromium emission sources.

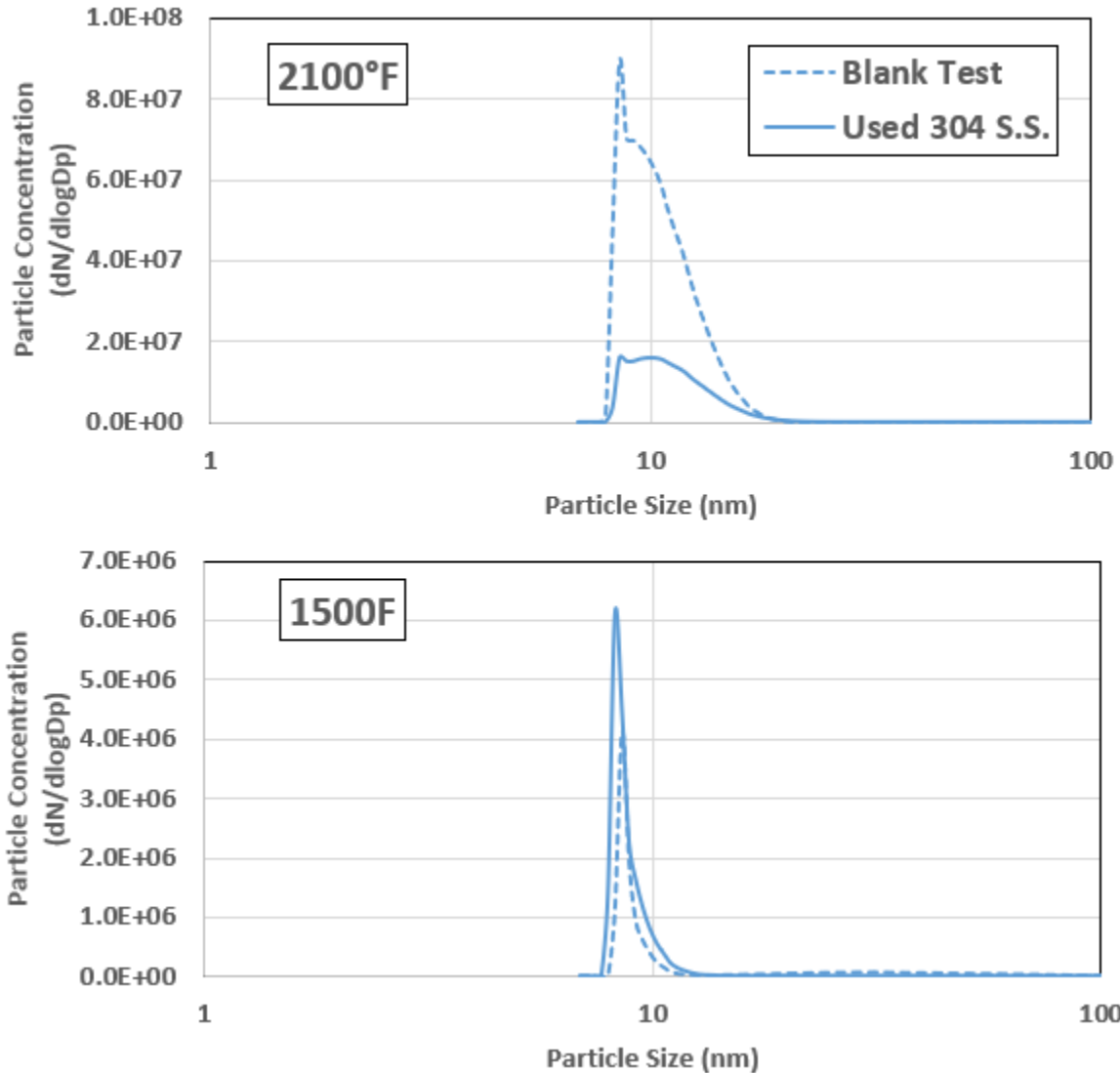


**Figure 10. particle number emissions as a function of furnace temperatures**

### 3.7 Particle size distributions

A TSI, Inc. scanning mobility particle sizer spectrometer (SMPS) was employed to measure the particle size distribution during the experiments with the 304 S.S. sample and sample blanks following the test sequence. For all tests, the majority of particles were below 20 nm in diameter (Figure 11). Blank tests showed increased particle populations compared to tests with the 304 S.S. sample at 2100°F. The opposite trend was observed during testing at 1500°F, with the loaded tests showing slightly higher particle concentrations at around 10 nm in diameter. More studies in this

area are necessary due to the fact that small particles in the 10 nm range can penetrate into lower lung airways (Schraufnagel, 2020).



**Figure 11. Particle size distributions**

### 3.8 Furnace Inventory

Furnace inventory information was obtained through SCAQMDs permitting and inspection databases, facilities survey responses, site visits, and internet searches. The inventory was built to look at facility name, type of work, controlled or uncontrolled atmosphere, dimensions/capacity,

types of alloys, operating temperatures, heat source, and heating capacity of all furnaces available in the southern California air basin. In total, this inventory accounted for 127 different heat-treating facilities in the the south coast air basin. Inside these facilities there are 597 furnaces with over 270 of these heat-treating materials with more than 1% chromium content. Temperatures of these furnaces can range from 200-2300°F. The inventory is in electronic form and available upon request.

## 4. Conclusions

The purpose of this study was to better understand the production of hexavalent chromium emissions from various heat-treating facilities in SCAB. An initial test plan was formed in order to answer fundamental questions about the process involved in hexavalent chromium emissions and how they might be mitigated in the future. As more test results were analyzed, the test plan was adjusted in order to better answer different questions that arised. This study was conducted in a laboratory setting using a high temperature gas heat treat furnace. A number of different materials were tested, including metals, refractory material, and furnace materials that are typical of heat-treating operations in SCAB. Testing on each material was performed at temperatures of 2100°F, 1900°F, and 1500°F. Rack, tray, and needle materials were also tested at 800°F to better understand hexavalent chromium formation at low temperature conditions. Several blank tests were also conducted at all temperature conditions to evaluate the degree of hexavalent chromium contamination in the furnace. The main findings of this study can be summarized as:

- Hexavalent chromium emissions were detectable starting at 1500°F.
- Hexavalent chromium emissions were strongly depended on temperature, surface area, and chromium content.
- The formation of scale and dust as a result of the heat-treating process can “season” or contaminate the furnace. Thus, high emissions of hexavalent chromium can be produced even from a heated furnace with no materials processed.
- Cleaning, extending heating periods with no metals, and furnace coats can be applied to reduce hexavalent chromium emisisions of “seasoned” furnaces.
- Increasing furnace temperatures led to an increase in sub-micron particles, CO<sub>2</sub>, and NO<sub>x</sub> emissions.

## References

- Bagchi, D. Cytotoxicity and Oxidative Mechanisms of Different Forms of Chromium. *Toxicology*, 180, 1, 2002, 5–22., doi:10.1016/s0300-483x(02)00378-5.
- Barceloux, Donald G., and Donald Barceloux. Chromium. *Journal of Toxicology: Clinical Toxicology*, 37, 2, 1999, 173–194., doi:10.1081/clt-100102418.
- Beukes, J.p., et al. Review of Cr(VI) Environmental Practices in the Chromite Mining and Smelting Industry – Relevance to Development of the Ring of Fire, Canada. *Journal of Cleaner Production*, vol. 165, 2017, pp. 874–889., doi:10.1016/j.jclepro.2017.07.176.
- Błasiak, Janusz, and Joanna Kowalik. A Comparison of the in Vitro Genotoxicity of Tri- and Hexavalent Chromium. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*, 469, 1, 2000, 135–145., doi:10.1016/s1383-5718(00)00065-6.
- Chen, Jyh-Cherng, et al. The Simulation of Hexavalent Chromium Formation under Various Incineration Conditions. *Chemosphere*, 36, 7, 1998, 1553–1564., doi:10.1016/s0045-6535(97)10053-4.
- Huang L., Yu C.H., Hopke P.K., Lioy P.J., et al. Measurement of soluble and total hexavalent chromium in the ambient airborne particle in New Jersey. *Aerosol Air Qual Res.* 2014, 14, 1939-1949.
- International Agency for Research on Cancer. List of Classifications - IARC Monographs on the Identification of Carcinogenic Hazards to Humans (2020), <https://monographs.iarc.fr/list-of-classifications/>.
- International Agency for Research on Cancer. Arsenic, Metals, Fibers and Dusts – Volume 100C, A Review of Human Carcinogens. IARC Monographs on the Identification of Carcinogenic Hazards to Humans. Lyon 2012.
- Linak, William P., et al. “Formation and Destruction of Hexavalent Chromium in a Laboratory Swirl Flame Incinerator.” *Combustion Science and Technology*, vol. 116-117, no. 1-6, 1996, pp. 479–498., doi:10.1080/00102209608935559.
- Mao, Linqiang, et al. “The Role of Temperature on Cr(VI) Formation and Reduction during Heating of Chromium-Containing Sludge in the Presence of CaO.” *Chemosphere*, vol. 138, 2015, pp. 197–204., doi:10.1016/j.chemosphere.2015.05.097.

- Nath, Mithun, et al. "Phase Evolution with Temperature in Chromium-Containing Refractory Castables Used for Waste Melting Furnaces and Cr(VI) Leachability." *Ceramics International*, vol. 44, no. 16, 2018, pp. 20391–20398., doi:10.1016/j.ceramint.2018.08.032.
- Nico, P.S., et al. Redox dynamics of mixed metal (Mn, Cr, and Fe) ultrafine particles. *Aerosol Sci. Technol.*, 43 (2009), pp. 60-70.
- Saha, Rumpa, et al. "Sources and Toxicity of Hexavalent Chromium." *Journal of Coordination Chemistry*, vol. 64, no. 10, 2011, pp. 1782–1806., doi:10.1080/00958972.2011.583646.
- Schraufnagel, D.E. The health effects of ultrafine particles. *Experimental & Molecular Medicine* 2020, 52, 311-317.
- Sokolov, V. A. "Problem of Hexavalent Chromium in the Production of Fusion-Cast Chromium-Containing Refractories." *Refractories and Industrial Ceramics*, vol. 53, no. 2, 2012, pp. 112–114., doi:10.1007/s11148-012-9474-6.
- Sun H., Brocato J., Costa M. Oral chromium exposure and toxicity. *Curr. Environ. Health Rep.* 2015, 2, 295-303.
- Świetlik, Ryszard, et al. "Chromium(III/VI) Speciation in Urban Aerosol." *Atmospheric Environment*, vol. 45, no. 6, 2011, pp. 1364–1368., doi:10.1016/j.atmosenv.2010.12.001.
- Tiwari A.K., Orioli S., De Maio M. Assessment of groundwater geochemistry and diffusion of hexavalent chromium contamination in an industrial town of Italy. *J. Contam. Hydrol.* 2019, 225, 103503.
- US EPA, Regional Screening Level (RSL) Subchronic Toxicity Supporting Table November 2019, <https://semspub.epa.gov/work/HQ/199660.pdf>
- Vaiopoulou E., Gikas P. Regulations for chromium emission to the aquatic environment in Europe and elsewhere. *Chemosphere* 2020, 254, 126876.
- Werner, M., et al. Laboratory study of simulated transformations of chromium in ultrafine combustion aerosol particles. *Aerosol Sci. Technol.*, 40 (2006), pp. 545-556.
- Wu, Yingjiang, et al. Formation Mechanisms and Leachability of Hexavalent Chromium in Cr<sub>2</sub>O<sub>3</sub>-Containing Refractory Castables of Electric Arc Furnace Cover. *Metallurgical and Materials Transactions B*, vol. 50, no. 2, 2019, pp. 808–815., doi:10.1007/s11663-018-1498-y.



Yu C.H., Huang L., Shin J.Y., Artigas F., et al. Characterization of concentration, particle size distribution, and contributing factors to ambient hexavalent chromium in an area with multiple emission sources. *Atmospheric Environment* 2014, 94, 701-708.

## Appendix A

I-625 is short for Inconel 625 and is a nickel based ‘superalloy’, characterized by high strength, excellent corrosion resistance and great fabricability. This alloy is typically used in one of two different heat-treated conditions, annealing or solution treating. A typical annealing cycle would be temperature of 1700°F for about 1 hour per inch of thickness once furnace recovers to temperature, followed by rapid air cooling or water quenching. A typical solution treating cycle includes temperatures of 2050°F for about 30 minutes per inch of thickness once furnace recovers to temperature, followed by rapid air cooling or water quenching. I-625 contains up to 23% chromium.

**Table A1: Limiting Chemical Composition of I-625**

<b>Element</b>	<b>Limiting Composition (Wt. %)</b>
<b>Nickel</b>	58.0 min
<b>Chromium</b>	20.0 – 23.0
<b>Iron</b>	5.0 max
<b>Molybdenum</b>	8.0 – 10.0
<b>Niobium + Tantalum</b>	3.15 – 4.15
<b>Carbon</b>	0.10 max
<b>Manganese</b>	0.50 max
<b>Silicon</b>	0.50 max
<b>Phosphorus</b>	0.015 max
<b>Sulfur</b>	0.015 max
<b>Aluminum</b>	0.40 max
<b>Titanium</b>	0.40 max
<b>Cobalt</b>	1.0 max

I-410 is a martensitic stainless steel characterized by high corrosion resistance and superior wear resistance. A typical heat treatment cycle is to austenitize at 1800°F for about 1 hour per inch of thickness once furnace recovers to temperature, followed by rapid air cooling. After, 410 is tempered at around 1075°F for about 2 hours per inch of thickness once furnace recovers to temperature, followed by air cooling. 410 contains up to 12 wt.% chromium.

**Table A2: Typical Chemical Composition of 410**

<b>Element</b>	<b>Typical Composition (Wt. %)</b>
<b>Carbon</b>	0.13
<b>Manganese</b>	0.50
<b>Silicon</b>	0.40
<b>Chromium</b>	12.0
<b>Iron</b>	Balance

N50 is short for Nitronic 50, also known as XM-19. It is a nitrogen-strengthened austenitic stainless-steel alloy with superior resistance corrosion and strength. A typical heat treatment cycle for N50 includes solution/annealing treatment at 2000°F for about 1 hour per inch of thickness once furnace recovers to temperature, followed by rapid air cooling or water quenching. N50 contains up to 23.5 Wt.% chromium.

**Table A3: Limiting Chemical Composition of N50**

<b>Element</b>	<b>ASTM A240 Limits (Wt. %)</b>
<b>Carbon</b>	0.06 max
<b>Manganese</b>	4.0 – 6.0
<b>Phosphorus</b>	0.040 max
<b>Sulfur</b>	0.030 max
<b>Silicon</b>	0.75 max
<b>Chromium</b>	20.5 – 23.5
<b>Nickel</b>	11.5 – 13.5
<b>Molybdenum</b>	1.50 – 3.00
<b>Columbium</b>	0.10 – 0.30
<b>Vanadium</b>	0.10 – 0.30
<b>Nitrogen</b>	0.20 – 0.40
<b>Iron</b>	Balance

17-4 precipitation hardening stainless steel is characterized by high strength and moderate level of corrosion resistance. A typical heat treatment cycle includes solution/annealing treatment at 1900°F for about 1 hour per inch of thickness once the furnace recovers to temperature, followed by rapid air cooling. After, 17-4 is heat-treated by aging/precipitation hardening at 1025°F for four hours once metal reaches temperature, followed by air cooling. 17-4 contains about 15.5% chromium

**Table 4: Typical Chemical Composition of 17-4**

<b>Element</b>	<b>Typical Composition (Wt. %)</b>
<b>Carbon</b>	0.04
<b>Manganese</b>	0.40
<b>Phosphorus</b>	0.020
<b>Sulfur</b>	0.005
<b>Silicon</b>	0.50
<b>Chromium</b>	15.5
<b>Nickel</b>	4.5
<b>Columbium + Tantalum</b>	0.30
<b>Copper</b>	3.50
<b>Iron</b>	Balance

310 S.S. is an austenitic heat resistant alloy with excellent corrosion resistance. It contains 24-26% chromium and 19-22% nickel.

**Table A5: Typical Chemical Composition of 310 SS**

<b>Element</b>	<b>Typical Composition (Wt. %)</b>
<b>Chromium</b>	24 - 26
<b>Nickel</b>	19.2 - 22
<b>Carbon</b>	.25 max
<b>Silicon</b>	1.5 max
<b>Manganese</b>	2 max
<b>Phosphorus</b>	.045 max
<b>Sulfur</b>	.03 max
<b>Molybdenum</b>	.75 max
<b>Copper</b>	.50 max
<b>Iron</b>	Balance

304 S.S. is the most common stainless steel. It is an austenitic stainless steel with Chromium between 15-20% and nickel between 2-10.5%.

**Table A6: Typical Composition of 304 SS**

<b>Element</b>	<b>Typical Composition (Wt. %)</b>
<b>Carbon</b>	0.08 max
<b>Manganese</b>	2.0
<b>Silicon</b>	0.75
<b>Phosphorus</b>	0.045
<b>Sulfur</b>	0.030
<b>Chromium</b>	18 – 20
<b>Nickel</b>	8.0 – 10.5
<b>Nitrogen</b>	0.10
<b>Iron</b>	Balance

RA 330 is a tray material used in common furnaces. It has good resistance to oxidation and nitridation and is easily welded. It contains chromium from 17-20% and nickel from 34-37%

**Table A7: Typical Chemical Composition of RA 330**

<b>Element</b>	<b>Typical Composition (Wt. %)</b>
<b>Carbon</b>	0.08 max
<b>Manganese</b>	2.0 max
<b>Phosphorus</b>	0.03 max
<b>Sulfur</b>	0.03 max
<b>Silicon</b>	0.75 – 1.50
<b>Chromium</b>	17 – 20

<b>Nickel</b>	34 – 37
<b>Molybdenum</b>	1.00 – 1.75
<b>Copper</b>	1.0 max
<b>Titanium</b>	1.9 – 2.3 max
<b>Iron</b>	Balance
<b>Tin</b>	0.025
<b>Lead</b>	0.005 max

HU is a heat resistant stainless steel used as tray material in common furnace applications. It contains 17-20% chromium and 37-41% nickel.

**Table A8: Typical Chemical Composition of HU**

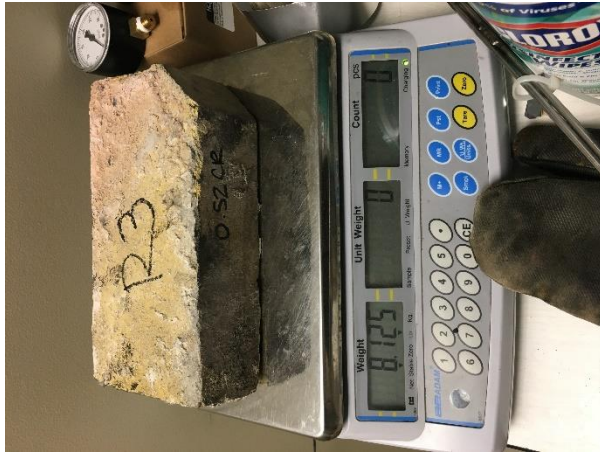
<b>Element</b>	<b>Typical Composition (Wt. %)</b>
<b>Carbon</b>	0.35 – 0.75
<b>Manganese</b>	0.0 – 2.0
<b>Chromium</b>	17 – 21
<b>Molybdenum</b>	0.0 – 0.5
<b>Nickel</b>	37 – 41
<b>Iron</b>	34.75 – 45.65

**Table A9: Materials given to UCR CE-CERT for Furnace Testing**

Punch Outs	
Material	Quantity
I-625	5
410	5
N-50	5
17-4	5
Refractory	
Material	Quantity
1	4
2	4
3	4
Racking/tray/needles	
Material	Quantity
310 S.S. Needles	0.905 lbs
304 S.S. Needles	1.015 lbs
304 SS Racking Material (used)	1
304 SS Racking Material (new)	1
HR9 racking Material (used)	1
HR9 racking material (new)	1
HU (used)	2
RA330 (used)	2

## Appendix B







**Appendix C**

Metal Sample ID	Material	Chrome Content	Weight	Height	Diameter	Surface Area
		Wt. %	lb	cm	cm	cm <sup>2</sup>
n/a	n/a					
1	I-625	20-23	5.085	3.7	9.9	269.03
2	I-625	20-23	9.495	6.7	10	367.57
3	I-625	20-23	7.415	5.8	10	339.29
4	I-625	20-23	6.13	4.8	9.6	289.53
5	I-625	20-23	6.815	5	10	314.16
6	N-50	20.5-23.5	3.91	3	10	251.33
7	N-50	20.5-23.5	9.72	7	10	376.99
8	N-50	20.5-23.5	6.335	4.3	10	292.17
9	N-50	20.5-23.5	5.595	4.5	10.2	307.62
10	N-50	20.5-23.5	6.18	4.8	9.8	298.64
11	410	~15.5	2.31	2.7	8.7	192.69
12	410	~15.5	2.855	3.5	8.6	210.74
13	410	~15.5	2.62	3.5	9	226.19
14	410	~15.5	2.585	2.4	8.6	181.02
15	410	~15.5	2.76	3.1	8.5	196.27
16	17-4	~12.0	1.345	2.7	7.1	139.41
17	17-4	~12.0	1.24	2.6	7.6	152.81
18	17-4	~12.0	1.62	2.6	6.9	131.15
19	17-4	~12.0	2.03	3.2	7	147.34
20	17-4	~12.0	1.265	2.2	7.1	128.26