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Shipbuilding and Ship Repair Industry Initiative to Prepare for and Comply with the U.S. EPA Residual Risk Ruling (RRR)



NSRP Joint Panel Meeting
Environmental Technologies SP-1 Panel &
Surface Preparation & Coating SP-3 Panel
Johnstown, PA
September 30, 2008





Project Objectives

- Ensure continued operations at shipyards pre/post RRR
- Determine current state of welding practices at shipyards
- Perform independent analysis of environmental risk model
- Identify and evaluate technologies/strategies to reduce welding emissions
- Support sustainable Technical Transition Plan



Project Team

- **Supporting Organizations**
 - National Shipbuilding Research Program (NSRP)
 - Advance Technology Institute (ATI)
 - Chief of Naval Operations (CNO), N45
 - Naval Sea Systems Command (NAVSEA)
 - Naval Surface Warfare Center Carderock Division (NSWCCD)
- **Navy Shipyards**
 - Norfolk Naval Shipyard (NNSY)
 - Puget Sound Naval Shipyard (PSNY)
- **Commercial Shipyards**
 - Atlantic Marine Alabama (AMA)
 - BAE Systems (San Diego and Norfolk Ship Repair)
 - Bath Iron Works (BIW)
 - General Dynamics (GD) National Steel and Shipbuilding Company (NASSCO)
 - Northrop Grumman Newport News (NGNN)
 - Northrop Grumman Ship Systems (NGSS) - PTR
- **Primary Contractor and Subcontractors/Consultants**
 - Concurrent Technology Corporation (CTC)
 - Applied Research Laboratory (ARL) - Penn State Univ.
 - Kelley Drye Collier Shannon, PLLC (KDCS)
 - Scientific Resources Associated (SRA)
 - SofTek Systems Inc. (SSI)
 - ATC Associates, Inc.



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Phased Approach

- **Phase 0 (January 2007 - July 2007)**
 - Fate and Transport of Emissions
 - Parallel modeling
 - Review of emission factor calculation procedures
 - Sampling and Analysis Plan for the Control Technology Demonstration
 - Speciation of Chrome Test Plan
- **Phase I (July 2007- July 2008)**
 - Emission Control Technology Demonstrations
 - Speciation of Chrome Evaluation



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Phase 0 Accomplishments

- Contacted 71 of the 86 shipyards listed in the NEI database to review and update their NEI data.
- Determined that Cr(VI) is the primary contaminant that influences the MIR for cancer.
- Determined that Mn is the primary metal risk driver for HI.
- Observed that Ni also influences the MIR for cancer, to a lesser extent than Cr(VI).
- Shipyards that submitted data corrections to the U.S. EPA showed a reduction in inhalation risks.
- Facilities should continue to closely monitor emissions, especially the Cr(VI), Mn, and Ni.



Phase 1 Accomplishments

- Constructed a modified weld fume chamber based on American Welding Society (AWS) specifications
- Conducted emission control technology demonstrations at the following shipyards:
 - Bath Iron Works: February 4-8, 2008
 - Atlantic Marine Alabama: February 18-22, 2008
- Conducted speciation of chromium testing at:
 - Concurrent Technologies Corporation's (CTC) Manufacturing Technology Facility (MTF): June 9, 2008
- Developed emission factors for various electrode/process combinations
- Determined the ratio of Hexavalent chromium to Trivalent chromium in emission from stainless steel welding
- Developed a decay rate constant for Hexavalent chromium emitted from stainless steel welding



Accomplishments Technology Transition

- Provided summary reports to ATI for potential distribution to U.S. Shipyards and NSRP ASE Program Representatives
 - Emission Parallel Modeling summary report
 - Welding Emission Calculation Procedures summary report
 - Control Technology Demonstration summary report
 - Speciation of Chromium summary report
 - Final Project Technical report
- Navy PM Engagement Plan
 - Provided project status high level quad chart to each shipyard POC for reporting up to their Navy PMs



Acknowledgements

- The NSRP for its sponsorship and support, and all of the residual risk project team members who provided valuable insight, information and direction throughout this effort.
- **Bath Iron Works**
 - Vince Dickinson, Stephanie Carver and Dean Brown
- **Atlantic Marine Alabama**
 - Terry Preston, Lindsey LeBlanc, Harry Harrelson, Rae Lawley and John Corley
- **The Lincoln Electric Company**



Emission Control Technology Demonstration Overview

- **Objectives**

- Determine emissions factors for Cr, Cr (VI), Mn, Ni, and Pb for the selected shipyard process/electrode combinations
- Determine capture efficiencies of 2 emissions control technologies

- **Approach**

- Collect, weigh and analyze weld fume generated in the Weld Fume Chamber
- Collect data on the amount of weld fume captured by the control technologies using a particulate matter probe

- **Anticipated Results**

- Evaluate existing U.S. EPA AP-42 emission factors or develop new emission factors for use by U.S. EPA
- Demonstrate the capture efficiency of the select control technologies



Weld Fume Chamber





Weld Fume Chamber

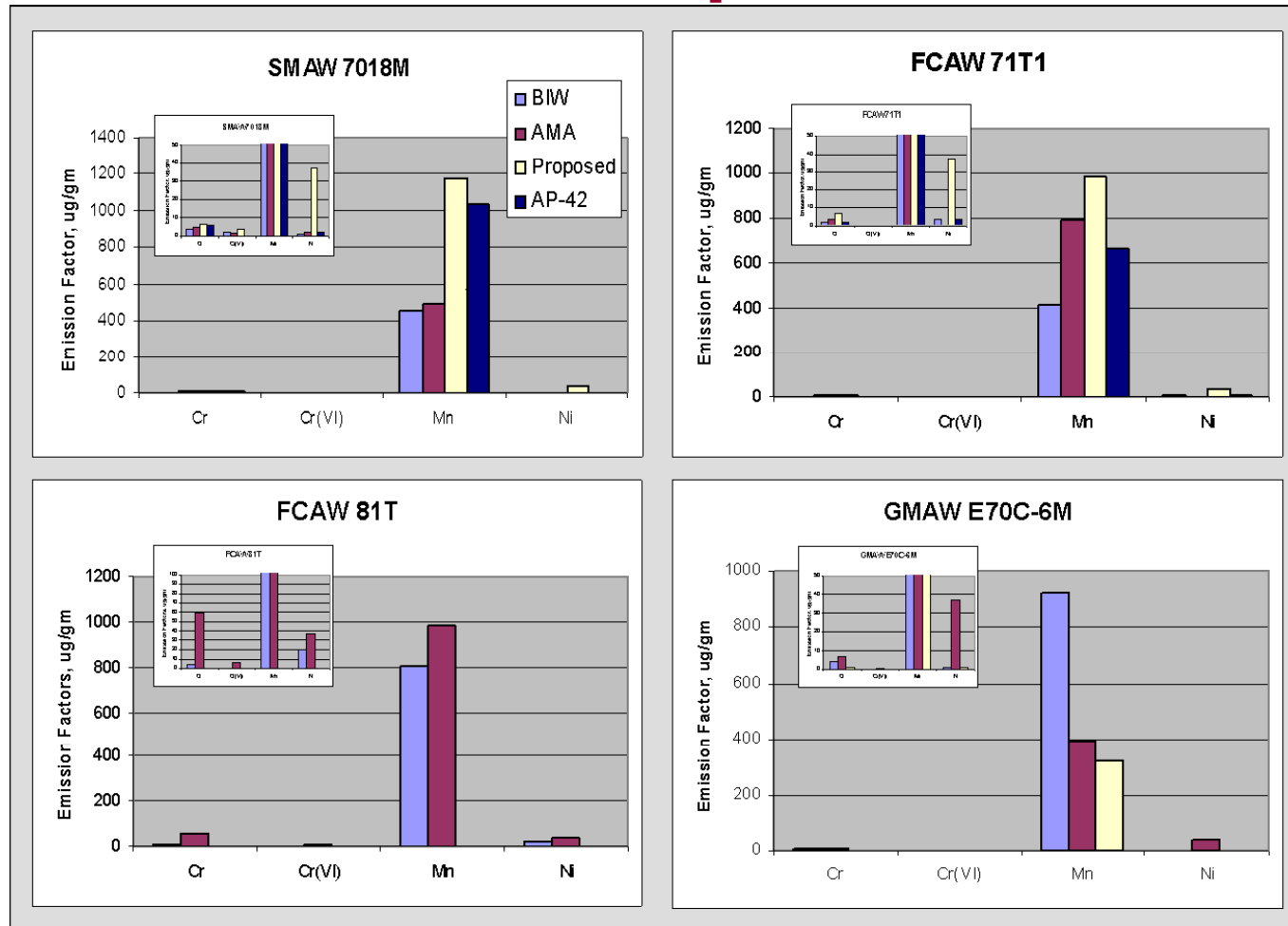
Emission Factors / Fume Generation Rates

- Conducted 5 welding runs for each selected process/electrode combination in the Weld Fume Chamber
 - Conducted gravimetric analysis on 5 filters
 - Analyzed 1 filter for Cr(VI)
 - Analyzed 1 filter for Total Metals
 - Analyzed 1 filter for Insoluble Ni
- Weld time averaged from 10-45 seconds depending on process/electrode combination
- Weld time was dependent on filter loading which caused a reduction in the flow rate
- Welding was stopped when the flow rate decreased to 26 CFM to stay in accordance with AWS specifications.



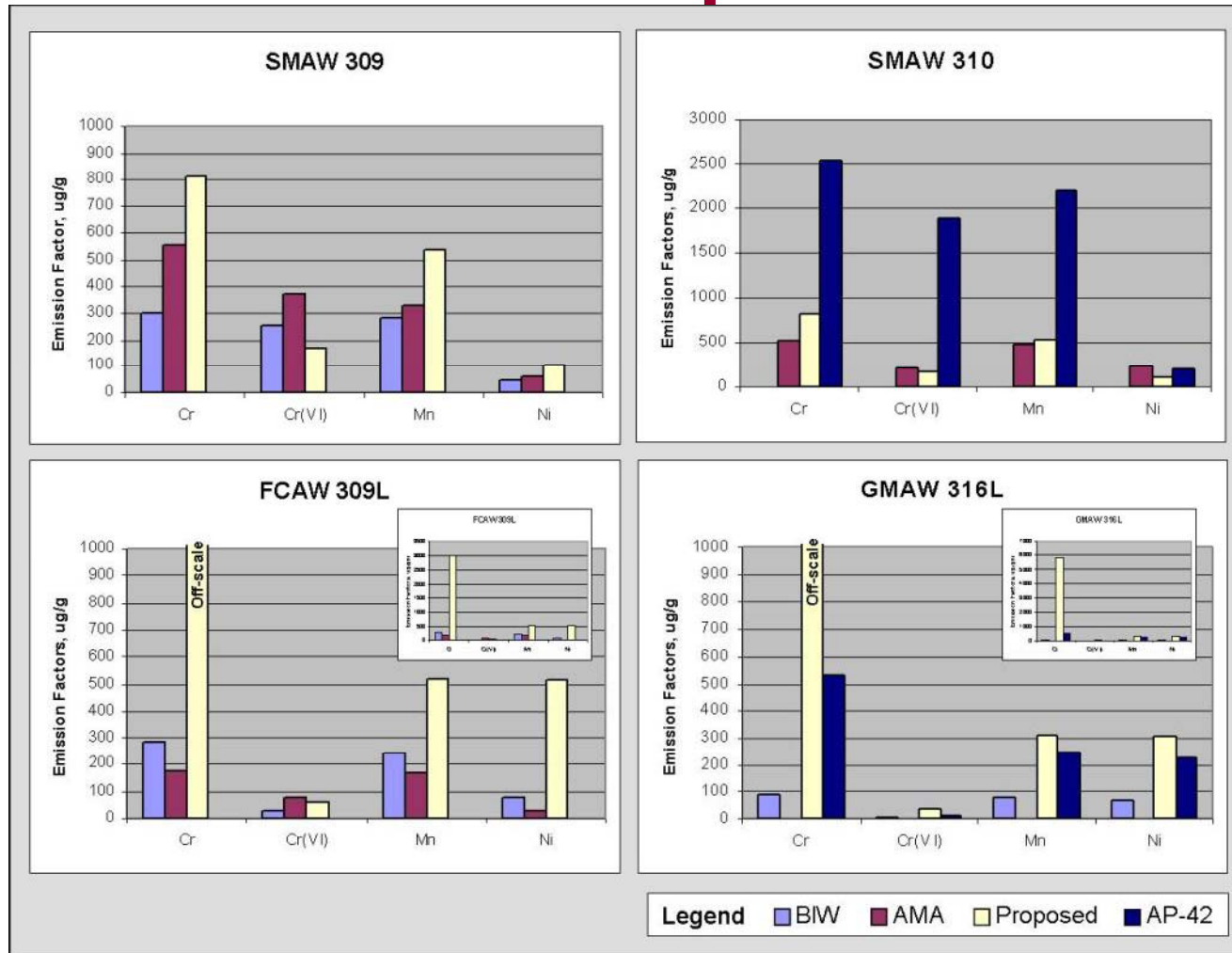


Carbon Steel Electrodes Emission Factor Comparison





Stainless Steel Electrode Emission Factor Comparison





Control Technologies Capture Efficiency

- Conducted 5 welding runs for each selected process/electrode combination with the following control technologies:
 - Miniflex with the EN-20 Nozzle was used for SMAW welding
 - Miniflex with the Fume Extractor Gun was used for FCAW and GMAW welding
 - Mobiflex was used with all process/electrode combinations
- Welding was conducted for 2 – 2 ½ minutes



Emission Control Technology Demonstration Materials

- **Control Technologies**
 - Miniflex (High Vac/Low Vol)
 - Mobiflex 200 (Low Vac/ High Vol)
- **Welding Processes and Electrodes**
 - Bath Iron Works
 - FCAW --- 71T1, 309
 - SMAW --- 7018, 309
 - GMAW --- 70C-8M, 316
 - Atlantic Marine Alabama
 - FCAW --- 71T1, 81T1, 309
 - SMAW --- 7018, 309, 310



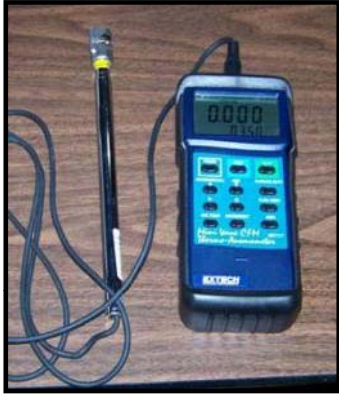
Miniflex with extraction attachments



Mobiflex 200-M
Low Vac/High Vol



Particulate Measurement



- Extech Anemometer
 - Recorded the average flow rate in Cubic feet of air per minute (CFM) over the run time

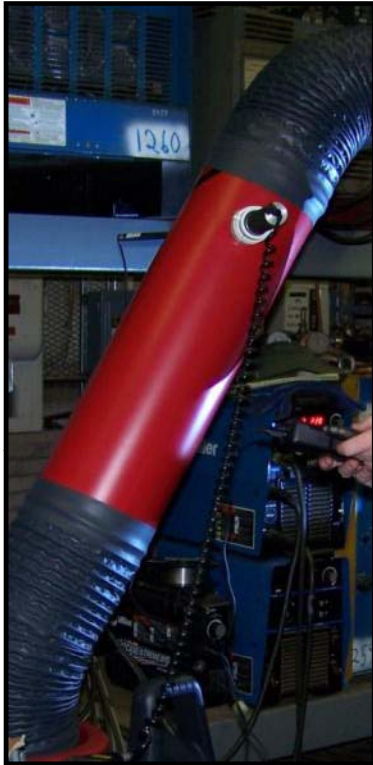


- Casella Microdust Pro particle analyzer
 - Recorded the average mg particulates/m³ air
 - Determined the correction factor (CF) and applied it to result to convert mg/m³ of Arizona road dust to mg/m³ of welding fume





Mobiflex 200



Control Technologies Capture Efficiency

Miniflex



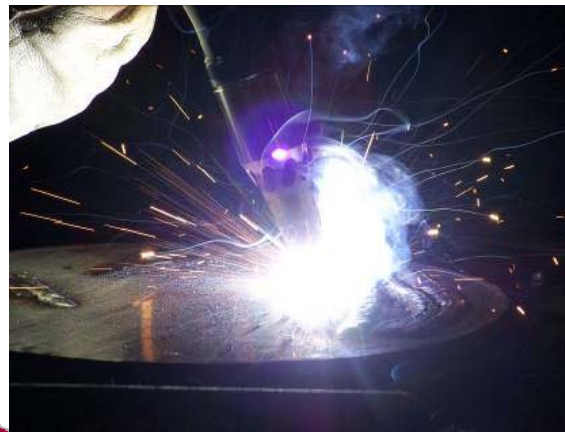
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Capture Efficiency



$$\text{Capture Efficiency} = \frac{\text{mg fume captured by CT} / \text{g weld rod consumed}}{\text{Total Fume Generated in Fume Chamber (mg/g)}} \times 100$$



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Mobiflex Capture Efficiency

Process	Electrode	Total Emissions		Emissions Captured		Capture Efficiency (% captured)	Shipyard
		mg/g electrode	Std Dev	mg/g electrode*	Std Dev		
SMAW	309L	6.62*	0.22	5.34	0.34	81	BIW
	309L	11.10 [†]	1.30	12.57	1.41	113	AMA
	7018M	12.29*	0.63	11.19	1.14	91	BIW
	7018M	13.33 [†]	0.42	13.94	1.03	105	AMA
	310-16	9.91 [†]	2.70	11.08	1.11	112	AMA
FCAW	71T-1C	10.27 [†]	1.43	7.47	0.44	73	AMA
	81T1	10.21 [†]	1.19	9.16	0.29	90	AMA

* Average of 5 runs

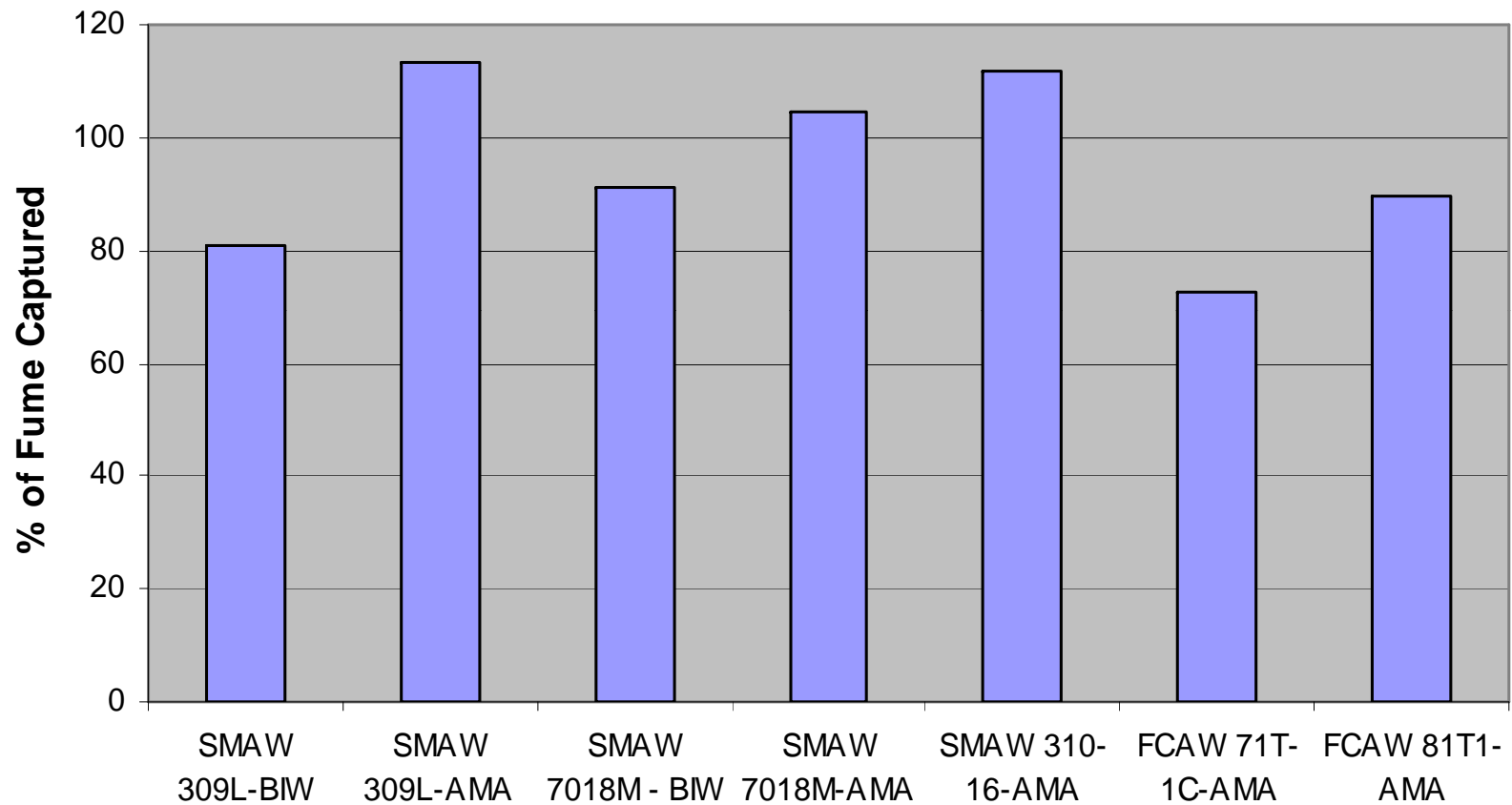
† Average of 4 runs



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Mobiflex Capture Efficiency



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Miniflex Capture Efficiency Data

Process	Electrode	Capture Device	Total Emissions		Emissions Captured		Capture Efficiency (% captured)	Shipyard
			mg/g electrode	Std Dev	mg/g electrode*	Std Dev		
SMAW	309L	EN20	6.62*	0.22	2.78	0.23	42	BIW
	309L	EN20	11.10 [†]	1.30	9.83	2.58	89	AMA
	7018M	EN20	12.29*	0.63	6.04	0.66	49	BIW
	7018M	EN20	13.33 [†]	0.42	7.92	0.86	59	AMA
	310-16	EN20	9.91 [†]	2.70	6.01	0.76	61	AMA

* Average of 5 runs

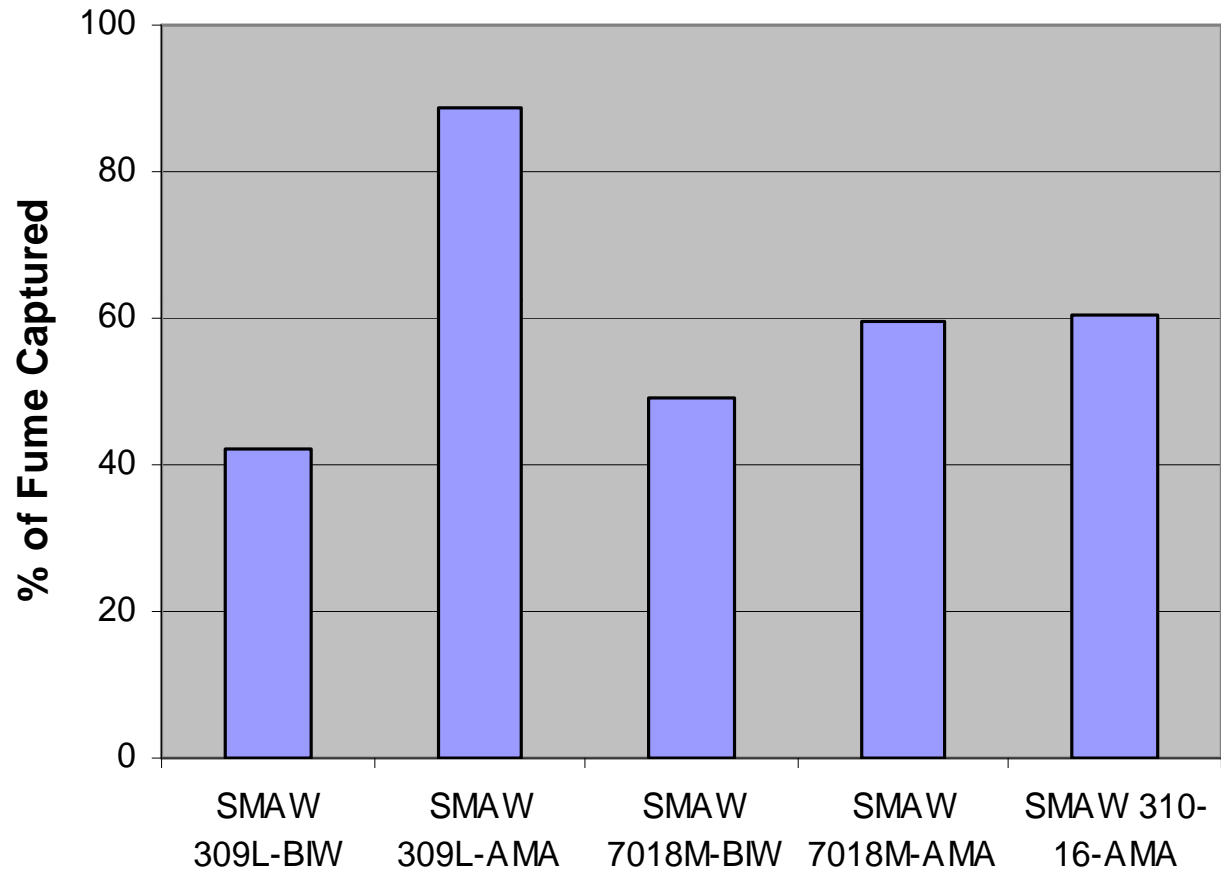
† Average of 4 runs



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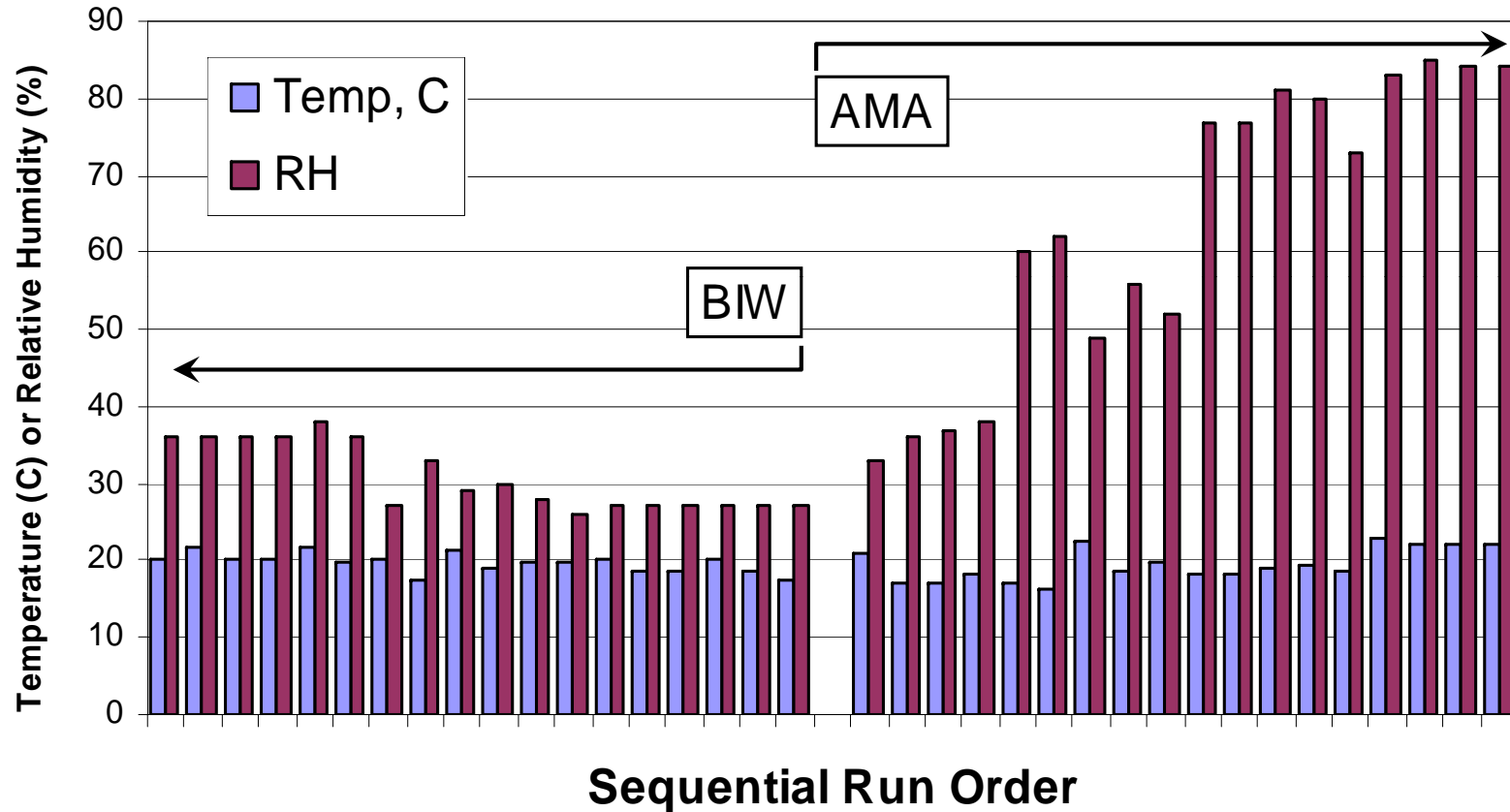
Miniflex Capture Efficiency EN20 Nozzle



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Field Conditions During Welding Runs



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Miniflex Fume Gun Test

FCAW, 71T1/0.052", AH36 carbon steel base plate, CO₂ shielding gas

100% suction
0% draft



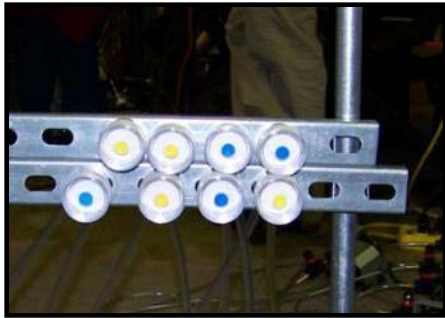
100% draft



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Effectiveness of Technologies



Miniflex

- Suspended eight 37 mm cassettes in CT exhaust stream
 - Pulled 4 LPM through each filter
 - Left in place throughout 5 welding runs of each stainless steel process/electrode combination, average sampling time 30 minutes
 - Analyze 4 filters for Cr(VI) and 4 for total metals

Mobiflex





Mobiflex Data

		Bath Iron Works					Atlantic Marine Alabama				
		Cr	Cr(VI)	Ni	Mn	Pb	Cr	Cr(VI)	Ni	Mn	Pb
		µg/sample					µg/sample				
SMAW	309L	<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
SMAW	310-16	This process/electrode combination was not tested at this shipyard					<1.5	<0.050	<0.17	<0.38	<1.8
							<1.5	<0.050	<0.17	<0.38	<1.8
							<1.5	<0.050	<0.17	<0.38	<1.8
							<1.5	<0.050	<0.17	<0.38	<1.8
FCAW	309L	<1.5	<0.050	<0.17	<0.38	<1.8	10	2.9	1.6	11	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	5.8	0.28	0.9	5.9	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	8	1.7	1.2	8.3	<1.8
		<1.5	<0.050	<0.17	0.56	<1.8	8	1	1.2	8.4	<1.8
GMAW	316L	<1.5	<0.050	<0.17	<0.38	<1.8	This process/electrode combination was not tested at this shipyard				
		<1.5	<0.050	<0.17	<0.38	<1.8					
		<1.5	<0.050	0.42	0.58	<1.8					
		<1.5	<0.050	0.43	0.58	<1.8					



Miniflex Data

		Bath Iron Works					Atlantic Marine Alabama				
		Cr	Cr(VI)	Ni	Mn	Pb	Cr	Cr(VI)	Ni	Mn	Pb
		µg/sample					µg/sample				
SMAW	309L	<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
SMAW	310-16	This process/electrode combination was not tested at this shipyard					<1.5	<0.050	<0.17	<0.38	<1.8
							<1.5	<0.050	<0.17	<0.38	<1.8
							<1.5	<0.050	<0.17	<0.38	<1.8
							<1.5	<0.050	<0.17	<0.38	<1.8
FCAW	309L	<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
		<1.5	<0.050	<0.17	<0.38	<1.8	<1.5	<0.050	<0.17	<0.38	<1.8
GMAW	316L	<1.5	<0.050	<0.17	<0.38	<1.8	This process/electrode combination was not tested at this shipyard				
		<1.5	<0.050	0.49	0.51	<1.8					
		<1.5	<0.050	<0.17	<0.38	<1.8					
		<1.5	<0.050	<0.17	<0.38	<1.8					





Control Technology Demonstration Accomplishments

- Provided efficiency data and associated cost information for two weld fume control technologies from Lincoln Electric
 - Miniflex was found to have an average capture efficiency of approximately 60% with the EN20 nozzle fume capture attachment
 - Mobiflex 200-M was found to have a capture efficiency of approximately 95%.
- Developed industry specific emission factors for total Cr, Mn, Ni, and Pb, for Cr(VI), and for insoluble Ni for eight welding process/electrode combinations.
 - Single-point emissions factors are either comparable to or significantly less than the emissions factors reported in AP-42 or the proposed residual risk emissions factors (*Serageldin, August 9, 2005*)
 - Factors were submitted to the U.S. EPA for potential use in regulatory reporting and future rule making decisions.
- Developed a procedure and the necessary equipment (fume chamber) for capturing 100% of welding emissions on filters acceptable for use in approved NIOSH and OSHA analytical methods. This can be used for future emission factor development.
- To our knowledge, and that of the U.S. EPA, this testing was the first attempt anywhere to measure the capture efficiency of weld fume control technologies. The knowledge gained in the development of these procedures will make it possible to evaluate additional control technologies in future studies.





Speciation of Chromium Study Overview

- **Objectives**
 - Determine Cr(VI) to Total Cr ratio present in weld fumes from 3 process/material combinations.
 - Determine the decay rate constant for Cr(VI) over 48 hours.
- **Approach**
 - **Determine Cr(VI) to Total Cr ratio**
 - Analyze fume for Cr(VI) using OSHA ID-215 method.
 - Analyze fume for Total Cr using NIOSH 7300.
 - **Determine Cr(VI) decay with respect to time**
 - Collect welding fumes on Tissuequartz fiber filters.
 - Preserve samples at time intervals of 3, 6, 9, ..., 48 hours.
 - Analyze samples for Cr(VI) using OSHA ID-215 method.
- **Anticipated Results**
 - Produce results that can be used to develop an accurate speciation profile for the Shipbuilding/Ship Repair Industry.
 - Estimate Cr(VI) decay with respect to time.
 - Evaluate existing U.S. EPA AP-42 emission factors or develop new emission factors for use by U.S. EPA.





Speciation of Chromium Study Materials

- Weld Fume Chamber



- Weld Process Material Combination

Process	Consumable	Size	Shielding Gas	Base Metal
FCAW	309L	.045	75/25 % Ar/CO ₂	316L
FCAW	71T-1	.052	100 % CO ₂	AH-36
SMAW	310-16	1/8	None	316L





Speciation of Chromium Study Sampling Weld Fume for Cr(VI) and Total Metals Analysis

- 6 individual welding runs were conducted for each of the FCAW and SMAW welding process/electrode.
 - During three of the welding runs, samples were collected on the pre-weighed and pretreated (NaOH) tissue quartz fiber filters for Cr(VI) analysis.
 - Three additional welding runs were conducted to collect samples on glass fiber filters to analyze for various metals, Cr, Fe, Cu, Ni, V, Pb, and Mn.
 - Blank runs, with the blower on for five minutes, with no welding taking place, were conducted before each change to a different type of electrode.
 - All analytical results were corrected based on the results of the blanks.



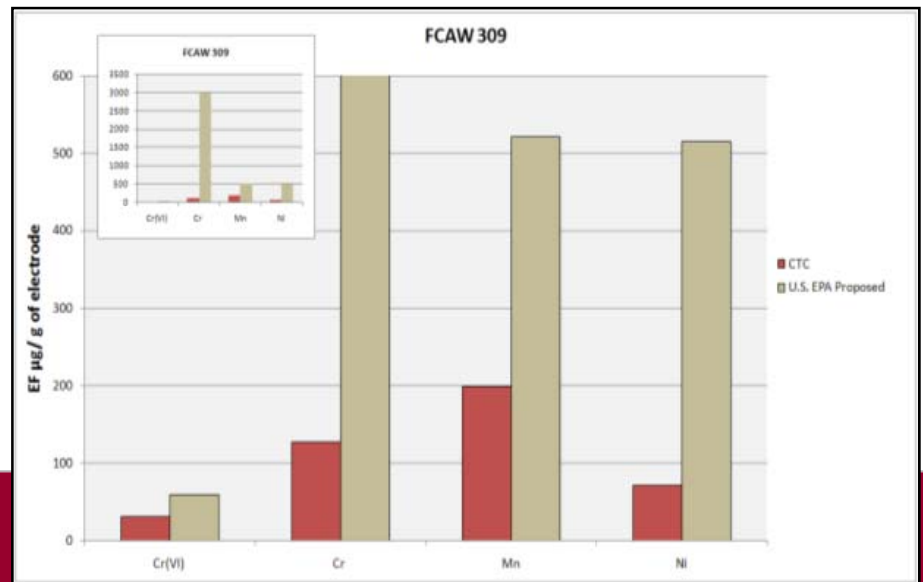
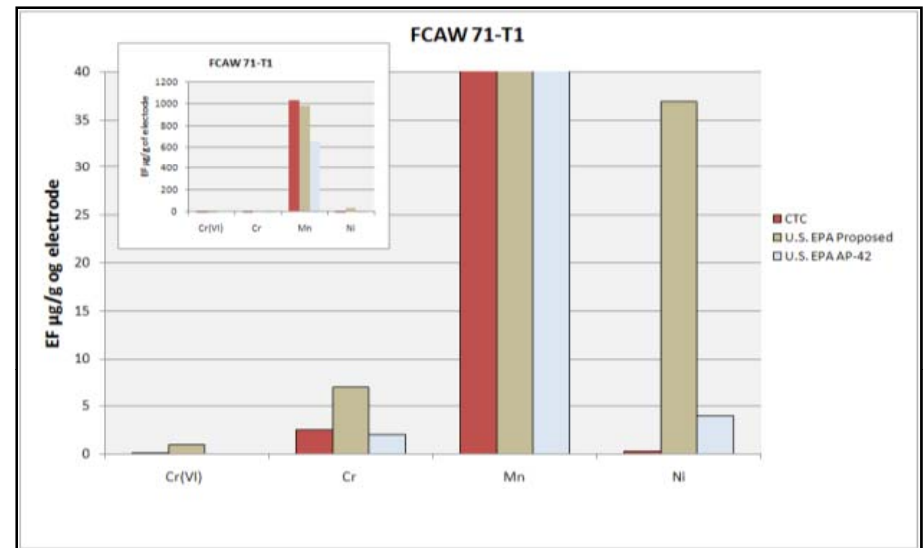
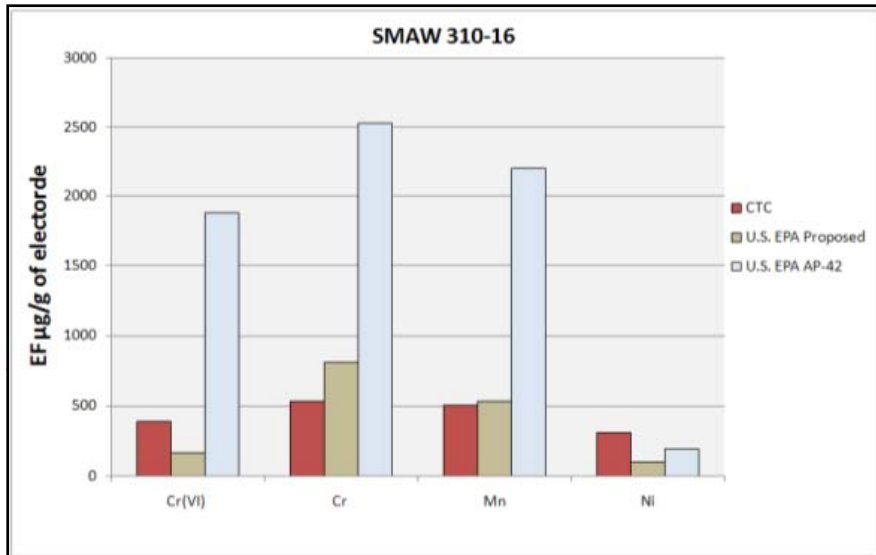
Speciation of Chromium Study Ratio of Cr(VI) to Total Cr

Process	Electrode Type	Cr(VI)/Cr (%)
SMAW	310-16	72
FCAW	309	25
	71T-1	3

- **Ratio of Cr(VI) to total Cr** = $[(\mu\text{g of Cr(VI)/g of electrode}) / (\mu\text{g of Cr/g of electrode})] * 100$
- The ratio of Cr(VI) to Cr(III) varied based on the various welding process/electrode combinations.



Comparison of Emission Factors to Current and Proposed U.S. EPA Emission Factors



- U.S. EPA AP-42**
SMAW 310, C-Rating
FCAW 71T, B-Rating
- CTC Developed**
- U.S. EPA RRR Proposed**



Comparison of Emission Factors to Current and Proposed U.S. EPA Emission Factors

- AP-42 emission factors were available for comparison to 7 of the developed emission factors
 - 4 out of the 7 developed emission factors lower in terms of μg emitted per gram of electrode
- RRR proposed emission factors were available for comparison to 12 of the developed emission factors
 - 9 out of the 12 developed emission factors were lower in terms of μg emitted per gram of electrode.



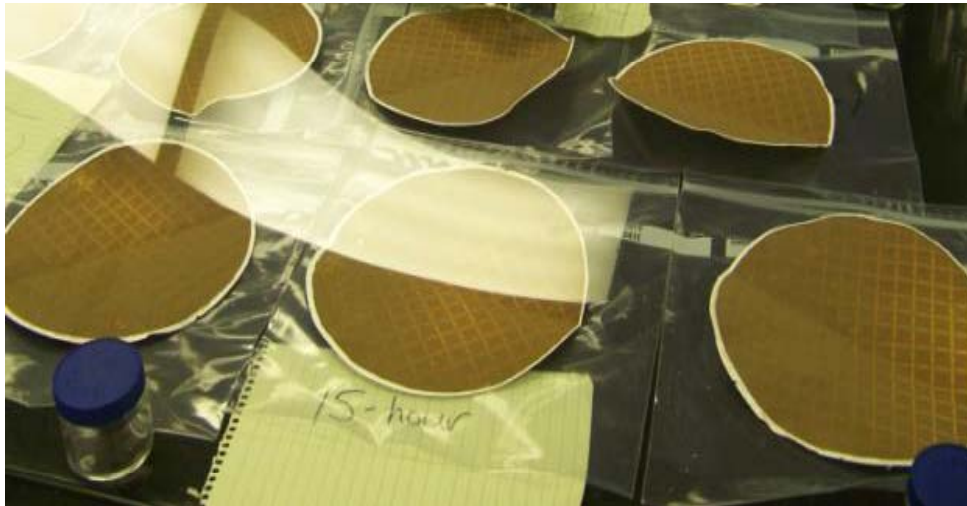
Speciation of Chromium Study

Sampling Weld Fume to Estimate Cr(VI) to Cr(III) Conversion

- 24 individual welding runs were conducted with the SMAW welding process/electrode combination., To provide consistency, the welding parameters were left the same for all runs.
- Fume samples were collected in sets of 3 to for each time interval of 3, 6, 9, 12, 15, 18, 24, or 48 hours after sampling.
- The samples were then exposed to fluorescent lighting and ambient temperatures in an environmentally-controlled laboratory for the designated period of time, ranging from 3 to 48 hours.
- At the designated time after sampling, each of the filters in a set of 3 were individually weighed and placed into a vial containing a sodium bicarbonate/sodium carbonate solution to quench the conversion of Cr(VI) to total Cr.



Speciation of Chromium Study Sampling Weld Fume to Estimate Cr(VI) to Cr(III) Conversion





Speciation of Chromium Study

Conversion of Cr(VI) to Cr(III) Over Time

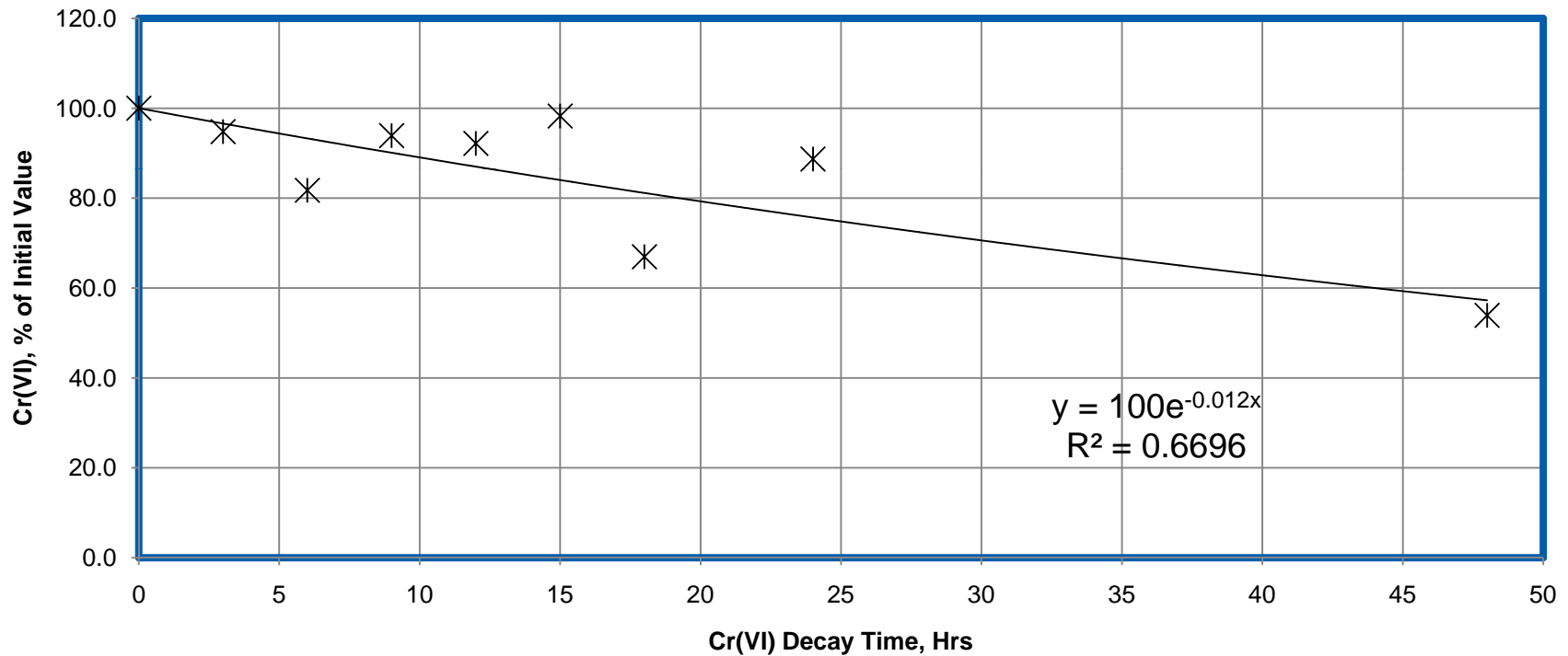
- Laboratory results were interpreted in three distinct ways to understand the decay of Cr(VI) with respect to time.
 - As-is-data (laboratory data as received from the laboratory in μg of Cr(VI) per sample)
 - Data normalized using the weld time (laboratory data normalized to 20 second weld time)
 - Data based on electrode consumed (μg of Cr(VI) per g of electrode consumed)
- If all variables (weld time, amount of electrode consumed, arc time, etc.) could have been eliminated, the results for all three approaches would have been identical. The study attempted to reduce variability in these parameters but some variation did occur.
- Examining the data using three approaches will provide a range of results that takes into account the variability of the experimental parameters.
- Prior to modeling analysis, the statistical “Q-Test” was conducted so that outliers could be identified and removed before calculating the rate constant.



Speciation of Chromium Study

Conversion of Cr(VI) to Cr(III) Over Time

Cr(VI) Decay Model: As-is-Data

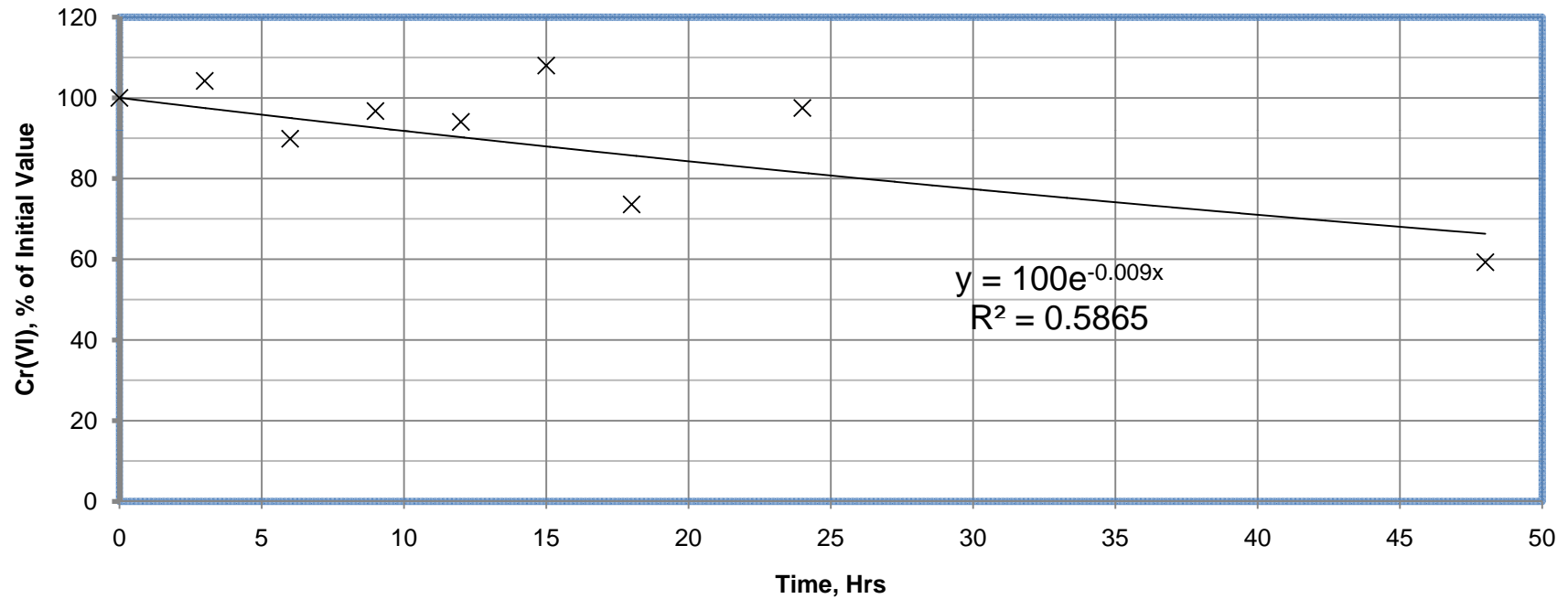




Speciation of Chromium Study

Conversion of Cr(VI) to Cr(III) Over Time

Cr(VI) Decay Model: Normalized Using
Weld Time (20 Sec)

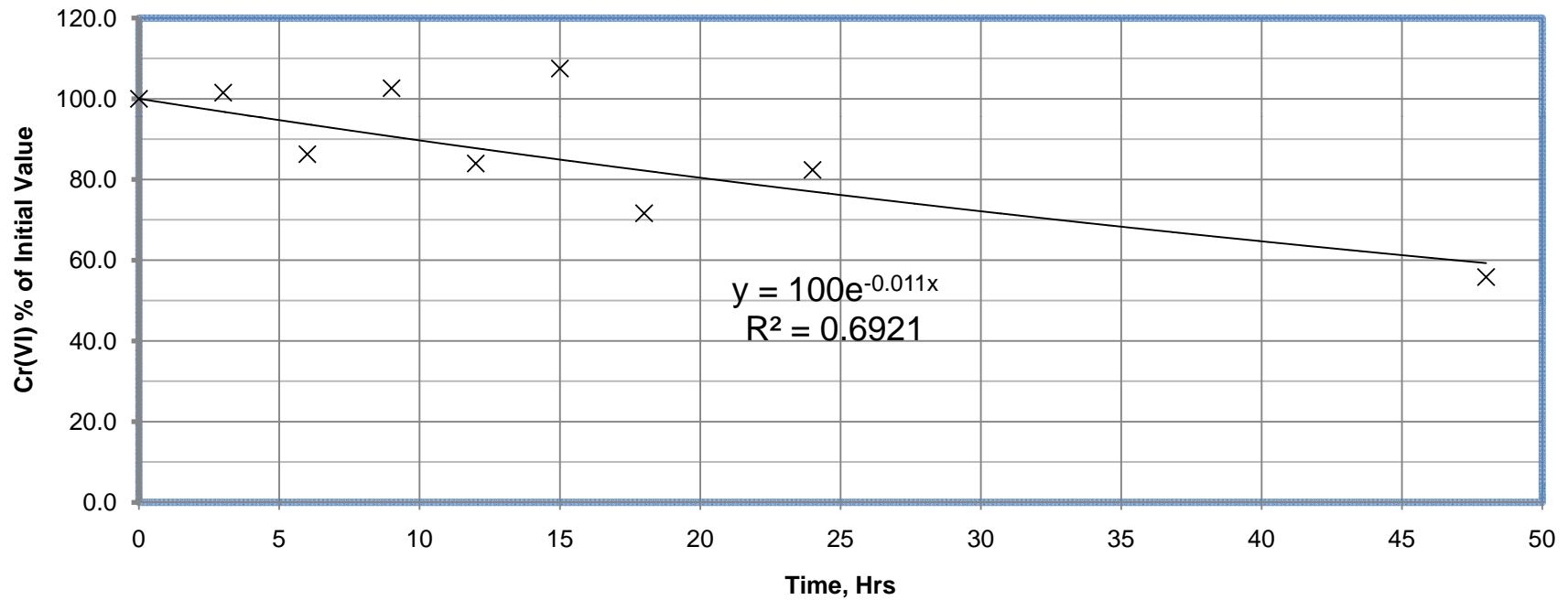




Speciation of Chromium Study

Conversion of Cr(VI) to Cr(III) Over Time

Cr(VI) Decay Model: Normalized Using
Weld Rod Mass



Summary of Results from the Three Calculation Methods

Data Analyses Method	Regression Coeff. (r^2)	Cr(VI) Decay Rate Constant (k)	Model Residual Value	Cr(VI) Half Life, Hrs	Cr(VI) % Decay in 24-hrs
As-is-Data	0.6696	0.012	9.3	57.5	25.0
Normalized Data based on Weld Time	0.5865	0.009	31.3	77.1	19.4
Normalized Data based on Weld Rod Mass	0.6921	0.011	20.4	63.0	23.2

- r^2 value closer to 1 indicates a stronger correlation between the X and Y variables as represented by the model
- A model residual value closer to 0 indicates a more uniform fit of the model to the data
- Larger 'k' value indicates a higher rate of Cr(VI) conversion to Cr(III)
- In terms of risk assessment, a smaller Cr(VI) half life will result in a higher % Cr(VI) decay thus a greatly reduced risk over time compared to a case involving a higher Cr(VI) half life value.



Speciation of Chromium Study

Conversion of Cr(VI) to Cr(III) Over Time

Results

- The calculated decay rate constant (k) for Cr(VI) in SMAW 310-16 weld fume ranged from 0.009 to 0.012, with an average of 0.0107.
- The resulting half-life ranged from 57.5 to 77.1 hours, with an average of 66 hours.
 - Based on these results, the expected amount of Cr(VI) to decay within 24 hours ranged from 19.4 to 25.0 %, with an average of 23.0%.
- Based on the comparison of the results, all three approaches produce similar decay rates and half-lives.
- “As-is-Data” was selected as the best approach to calculate the decay rate constant
 - Residual value closest to zero.
- When using the “As-is-Data” approach,
 - The model predicts that 25% of the initial Cr(VI) decays within 24 hours, and 44% of the initial Cr(VI) decays within 48 hours.
 - The Cr(VI) half-life is estimated to be approximately 58 hours.



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