

## Determination of Chromium Content in Carbon Steel Pipe of NPP using ICP-AES

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A method is proposed for determining chromium content in the carbon steel pipes of a nuclear power plant (NPP) to evaluate wall thinning caused by flow-accelerated corrosion (FAC). A flat file was used to obtain filings samples. To assess sampling quality, a disk form of SRM 1227 was ground with the flat file, and the amount of Cr in the filings was determined by ICP-AES. The content of chromium in the filings of SRM 1227 was estimated as six times higher than the certified value due to the contamination of chromium in the file. To eliminate chromium contamination from the file, it was coated with WC-12Co using high-velocity oxygen-fuel (HVOF) spraying systems. After obtaining filings samples using the coated file, Cr content in four types of disk-form SRMs was determined by ICP-AES. The recoveries of Cr in the disk-form SRMs were in the range of 95.4-102.6%, with relative standard deviations from 0.43 to 3.0%. The Cr contents in the filings collected from the used outlet headers of the nuclear power plants using the flat file coated were in the range of 0.11-0.19%.

**Key Words :** Chromium, Flow-accelerated corrosion (FAC), Coated file, High-velocity oxygen-fuel (HVOF), ICP-AES

### Introduction

The chemical composition of steel is one of the factors affecting the rate of flow-accelerated corrosion (FAC). Generally, chromium (Cr) content as low as 0.10% in carbon steel can significantly reduce the FAC rates, due to the high corrosion resistance of Cr.<sup>1</sup> Chromium content can be measured by energy dispersive X-ray analyzer (EDAX), X-ray fluorescence spectrometry (XRF), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS). Atomic Energy of Canada Limited (AECL) recommended using ICP-AES, ICP-MS or AAS for the determination of chromium content in the carbon steel used in the fabrication of outlet headers.<sup>2</sup> ICP-AES was selected due to advantages such as a wide dynamic range, high sensitivity, freedom from matrix interference, and multi-element analysis capability.<sup>3</sup>

FAC occurs in the pressure vessels of fossil fuel, industrial, and nuclear power plants. FAC is a pipe degradation process that occurs due to chemical corrosion accelerated by flowing water or a water-steam mixture.<sup>4-8</sup> Specifically, a protective hematite (Fe<sub>2</sub>O<sub>3</sub>) or magnetite (Fe<sub>3</sub>O<sub>4</sub>) layer on the carbon steel dissolves into a stream of flowing water or wet steam. This process reduces or eliminates the oxide layer and causes removal of base material. The remaining material is thinner and may, ultimately, suddenly rupture. Consequently, to prevent disastrous failures caused by FAC, several papers on key parameters which affect the rate of FAC including hydrodynamic,<sup>9-13</sup> environmental<sup>14</sup> and metallurgical factors<sup>15</sup> have been reported.

In this study, sampling methods in the field of nuclear

power plants are an important subject to determine chromium content in used pressure vessels for evaluation of wall thinning caused by FAC. A flat file is a good tool to obtain filings samples of pipe systems made from carbon steel in a nuclear power plants. Because the content of Cr in the flat file was shown to be very high in preliminary tests, it was concluded that it should not be used for the collection of samples. To prevent chromium contamination from the file, there are two ways. One is using a suitable file made of very hard steel, with Rockwell hardness C (HRC) greater than 72. The other is utilizing a file coated with WC-12Co by a high velocity oxygen-fuel (HVOF) spraying system.<sup>16</sup> The other was selected for collecting filings samples, and the Cr content in used outlet headers from nuclear power plants was determined using ICP-AES.

### Experimental

**Instrumentation.** A sequential ICP-AES (Activa M; Horiba Jobin Yvon SAS, Longjumeau, France) was used to measure Cr in the dissolved solution samples. Tungsten (W) content was also determined using a sequential ICP-AES (Ultima 2C; Horiba Jobin Yvon SAS) due to a higher sensitivity than the Activa M instrument. The operating conditions for determination of elemental content are shown in Table 1. An ST-4000 HVOF system (Eutectic Castolin Co., Inchon, Korea) was used to coat a flat file with WC-12Co. A carbon (C) and sulfur analyzer (CS800; Eltra GmbH, Neuss, Germany) was used to measure the C content in the filings of the standard reference materials (SRMs) that were ground using the flat file coated with WC-12Co. The Rockwell hardness C of the disk-form of SRMs and the flat

**Table 1.** Operating conditions of the ICP-AES

Item	Conditions
System	Sequential type (Activa M) Combination of sequential and simultaneous type (Ultima 2C)
Focal length	0.64 m (Activa M) 1 m (sequential type of Ultima 2C)
Mounting	Czerny-Turner
Grating	Dual 4324/2400 grooves (Activa M) Double order of 2400 grooves (sequential type of Ultima 2C)
Detector	Charge-coupled device (CCD) (Activa M) Photomultiplier tube (PMT) (Ultima 2C)
Power	1000 W
Torch	Fassel-type
Nebulizer	Meinhard TR 50-C1
Spray chamber	Cyclone-type
Plasma gas flow rate	12 L min <sup>-1</sup>
Coating gas flow rate	0.2 L min <sup>-1</sup>
Auxiliary gas flow rate	0 L min <sup>-1</sup>
Nebulizer flow rate	1 L min <sup>-1</sup>
Nebulizer pressure	3 bars

file before and after coating was measured by a Rockwell hardness tester (270 VRSD; AFFRI Corp., Italy) under 150 kgf on a 120° diamond cone indenter. X-ray diffraction (XRD) patterns of the flat file coated with WC-12Co were determined using a Siemens D5000 diffractometer (Siemens, Munich, Germany), with Cu K $\alpha$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ) at 40 kV and 40 mA with a scanning rate of  $2\theta = 1.2^\circ \text{ min}^{-1}$  from 20° to 80°.

**ICP-AES Analysis.** The analysis was performed in triplicate using a two-point calibration. The wavelengths for the measurement of the elements, along with the background position, the LOD, and the LOQ are listed in Table 2. The limit of quantification (LOQ) is defined as the concentration value corresponding to 15 times the standard deviation of the 0.1 M HNO<sub>3</sub> blank solution.<sup>17</sup>

**Reagents and SRMs.** The chemicals used, including HCl (Merck, Darmstadt, Germany), HF (Merck), HNO<sub>3</sub> (Merck), H<sub>2</sub>O<sub>2</sub> (Merck), and acetone (Merck) were of analytical grade. Distilled and demineralized water (DDW), with a specific resistance of 18.5 M $\Omega$ ·cm, was prepared using a Milli-Q plus Ultra Pure Water System (Millipore, Billerica, MA, USA). The concentrations of Cr and W (Spex CertiPrep, Metuchen, NJ, USA) in the stock solutions were

1,000 mg L<sup>-1</sup>, and the concentration of Fe (Spex CertiPrep) in the stock solution was 10,000 mg L<sup>-1</sup>. Cr and W stock solutions were diluted to prepare working standard solutions. To examine the effect of iron (Fe) concentration on the Cr intensity, solutions containing synthetic Fe and Cr were made by adding 0, 2.5, 5, 10, and 20 mg of Fe and 2  $\mu\text{g}$  of Cr to a 10 mL volumetric flask. Chip and disk forms of carbon steel standard reference material (SRM) were purchased from the National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA). Flat files and a diamond needle file were purchased from Samic THK Co. (Daegu, Korea). The coating material was a WC-727-1/1342 VM, WC-12Co agglomerated and sintered powder, prepared by Praxair (Danbury, CT, USA).

**Sample Collection.** Sandpaper was used to remove oxide on the carbon steel pipe, and the surface of the pipe was washed with acetone. To obtain filings samples of the pipe systems made from carbon steel in nuclear power plants, a flat file coated with WC-12Co was used. The different coated flat file was used for different sampling location to prevent contamination. An envelope taped to the pipe just below the sampling location was used to collect the filings samples.

**Dissolution of the Filings SRM and Samples.** Approximately 0.1 g of the filings SRM was transferred to a polypropylene beaker, and 12 mL of concentrated aqua regia was added to the beaker. The filings SRM was heated on a hot plate, and 0.5 mL of H<sub>2</sub>O<sub>2</sub> and 5 drops of HF (approximately 0.1 mL) were added to the beaker.<sup>18</sup> The solution was diluted to 50 mL with DDW in a polypropylene volumetric flask. Due to the presence of insoluble matter, the solution was filtered using Whatman filter paper before the measurements of Cr and W by ICP-AES. The samples were treated using the same procedure applied to the SRM.

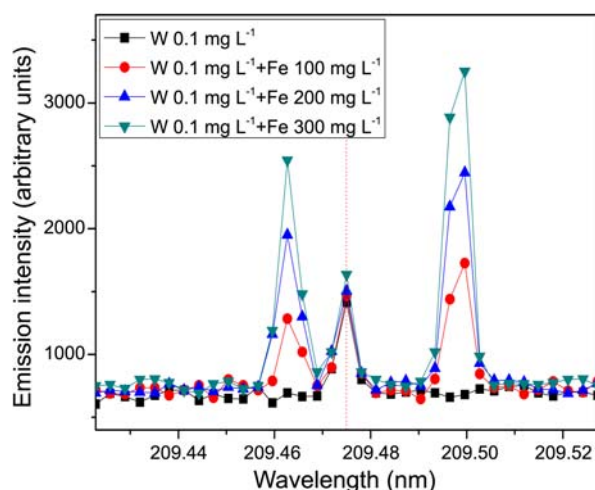
## Results and Discussion

**Investigation of Cr, Fe and W Analysis Lines.** The Fe matrix did not cause spectral interference for the most sensitive wavelengths for Cr, 205.571 and 206.164 nm, using ICP-AES (Activa M). However, these Cr wavelengths are not in agreement with the 205.552 and 206.149 nm reported in the Massachusetts Institute of Technology (MIT) Wavelength Tables, which collect over 100,000 wavelengths from molybdenum (200.004 nm) to cobalt (999.97 nm) by electric arc, spark, or discharge atomization sources.<sup>19</sup> On the other hand, Horiba Jobin Yvon (HJY) established a spectral line atlas for ICP-AES analysis using a spectrometer purged with nitrogen, a 0.64 m focal length, and a charge-coupled device (CCD) detector. Based on the HJY spectral line atlas, both observed lines of Cr, 205.571 and 206.164 nm, were shifted slightly from the reported values of 205.552 and 206.149 nm, respectively.<sup>19</sup>

Wünsch examined spectral interference in the determination of W content in the range of 0.02-80% in steel and other alloys using ICP-AES.<sup>20</sup> Based on the experimental results, the recommended analysis lines for W in an iron matrix

**Table 2.** Analytical wavelengths and detection limits

Element	Wavelength (nm)	Background position (nm)	Detection limits (ng mL <sup>-1</sup> )	
			LOD (3 $\sigma$ , $n = 10$ )	LOQ (15 $\sigma$ , $n = 10$ )
Cr	205.571	+0.03259	1.5	7.5
Cr	206.164	-0.04018	1.7	8.5
W	207.911	-0.02900	4.2	21.0

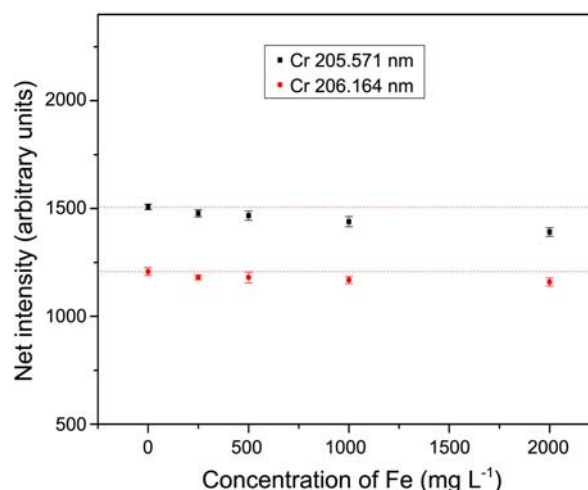


**Figure 1.** Wing spectral interference of Fe 209.463 nm on the W 209.475 nm analysis line.

were 400.875 and 207.911 nm. Although Wunsch recommended these W analysis lines in steel,<sup>20</sup> the 400.875 nm line could not be used in this study, due to the low content of W in the filings. The 207.911 nm line is the most sensitive wavelength, and the Fe matrix did not cause spectral interference with this line.

Another analysis line, 209.475 nm, of W using ICP-AES (Ultima 2C) was examined because this ICP-AES has good sensitivity and was not previously investigated by Wunsch.<sup>20</sup> Analysis showed the 209.475 nm analysis line of W had wing spectral interference, caused by the 209.463 nm wavelength of Fe, although the 100 mg L<sup>-1</sup> of Fe was concomitant with W (Figure 1). Moreover, neither of the Fe wavelengths, at 209.463 and 209.500 nm, are listed in the MIT Wavelength Tables.<sup>19</sup> However, ICP-AES confirmed that both wavelengths were emitted from the excited state of singly ionized iron, and these lines were slightly shifted, from 209.464 and 209.498 nm, compared with the iron lines reported by Michaud and Mermet using inductively coupled argon plasma.<sup>21</sup> On the other hand, neither line has been reported in neutral or singly ionized iron emission lines between the 160 and 250 nm wavelength region, by Grimm-type glow discharge plasma.<sup>22</sup>

**Effect of the Fe Matrix on the Cr Intensity.** Although ICP-AES has the advantage of freedom from matrix interference, the effect of the Fe concentration on the Cr intensity was examined because of the high concentration ratio of Fe to Cr. The analysis was carried out in three replicates. As shown in Figure 2, the net emission intensity of Cr at both wavelengths was not significantly influenced by Fe up to concentrations of 500 mg L<sup>-1</sup>. For solutions containing 0.2 mg L<sup>-1</sup> of Cr and 500 mg L<sup>-1</sup> of Fe, the net intensity of Cr decreased to less than 3.0% of the net intensity for the pure Cr standard solution containing 0.2 mg L<sup>-1</sup> of Cr for both analysis lines of Cr. In case of Cr coexisted with Fe 1000 mg L<sup>-1</sup>, the net intensity of Cr decreased to higher than 5.0% compared with that of the pure Cr standard solution for 205.571 analysis line of Cr. Therefore the concentration of



**Figure 2.** Effect of Fe concentration on Cr intensity.

Fe in the dissolved sample solution should not exceed 500 mg L<sup>-1</sup> to reduce the effect of Fe on Cr measurements using ICP-AES.

**Sample Collection.** To grind the surface of the carbon steel pipe for sample collection, the surface of a file needs a Rockwell hardness C (HRC) greater than 72. Because no information was available on the chemical composition and toughness of the abrasive wear for the flat file, preliminary tests were conducted. A disk-form of SRM 1227 was ground with the flat file, and the amount of Cr in the filings was determined using ICP-AES. As shown in Table 3, the results of the Cr content were about six times higher than the certified values. Because the experimental results for Cr content were so high, the content of chromium in the file was independently measured to identify contamination from the file. Indeed, the measured chromium content in the files was 0.63%, which much higher than the chromium in the samples, approximately 0.1-0.2%. Thus, the flat file could not be used for sample collection. To grind the surface of the NPP carbon steel pipe for sample collection, we tested a diamond needle file for the measurement of Cr in the filings of the disk-form of SRM 1227. It was found to be 265 μg g<sup>-1</sup>, which was 1.4 times higher than that of the certified value.

**Table 3.** Analytical results for Cr in a SRM 1227 ground using a flat file

N	Cr (μg g <sup>-1</sup> )		
	Certified	Found	
		205.571 nm	206.164 nm
1		1189	1189
2		1127	1124
3		1082	1082
X	190	1133	1132
SD	30 <sup>a</sup>	54	54
RSD		4.7	4.8
Relative error (%)		496	496

<sup>a</sup>Uncertainty

**Table 4.** Analytical results for Cr in SRMs ground using a flat file coated with WC-12Co

SRM No	Cr (%)		Relative error (%)
	Certified	Found <sup>a</sup>	
1264a	0.06 <sub>6</sub>	0.063 ± 0.001	-4.5
1269	0.201 ± 0.009	0.201 ± 0.006	0.0
1226	0.467 ± 0.005	0.468 ± 0.002	2.1

<sup>a</sup>*n* = 3

Thus, the diamond needle file also could not be used for sample collection.

Due to the high presence of Cr in the flat file made in Korea, the surface of the flat file was coated with WC-12Co using the HVOF spray system to prevent chromium contamination. To examine the effect of number of coating on the Cr content, the flat file was coated with WC-12Co once and three times, respectively. Because the amount of chromium content in the filings of SRM 1227 by a file coated once and three times was  $195 \pm 2$  (*n* = 3) and  $198 \pm 2$  (*n* = 3)  $\mu\text{g g}^{-1}$ , respectively, the number of coating did not affect the analytical results of chromium content based on the certified value,  $190 \pm 30 \mu\text{g g}^{-1}$ . Consequently, the file coated once was used for sample collection, and the results for Cr content determined using ICP-AES in three kinds of disk-form SRMs were in good agreement with the certified values (Table 4). Therefore, the problem of contamination from the chrome steel of the flat file was solved.

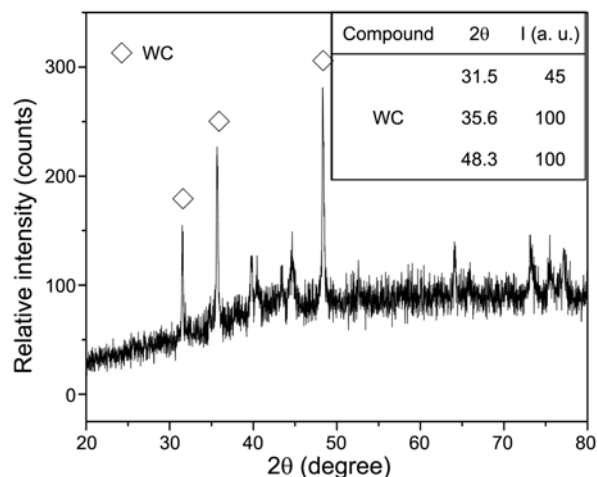
To investigate the relationship between the amount of C and W in the filings of SRMs and hardness, HRC values of the disk form SRMs were measured using a Rockwell hardness tester. The HRC values were in the range of HRC 11.3–23.8. As readings below HRC 20 are generally considered unreliable, the HRB of SRM 1269 was measured ( $93.0 \pm 1.3$ ; *n* = 6). It was hypothesized that the amount of C and W in the filings would decrease with increasing HRC. As shown in Table 5, however, no relationship was observed between the amount of C and W abraded and the hardness in the higher ranges of HRC. Because the results for the Cr content in the filings of SRM 1227 were about six times higher than the certified values (Table 3), the HRC of the file prior to coating was measured. It was found to be  $63.6 \pm 1.5$  (*n* = 8), which was less than HRC 72. After coating the file with WC-12Co, using the HVOF spray technique, the HRC of the file increased, to  $70.0 \pm 2.0$  (*n* = 10). Although the HRC results for the file after coating might be inappropriate because a macro-hardness tester was not used, the problem

of chromium contamination could be solved (Table 4).

Additionally, the carbon and tungsten contents in the filings of SRMs were measured to check the toughness of the abrasive wear for the flat file coated with WC-12Co. The cobalt content of the coating material in the filings of SRMs was not measured. As shown in Table 5, the amount of carbon and tungsten content due to contamination from the coating material in the filings of three kinds of SRMs was  $0.079 \pm 0.029\%$  and  $0.074 \pm 0.011\%$ , respectively. That is, the average mole percent of the carbon and tungsten content abraded from the coated flat file was 0.0066% and 0.0004%, respectively. It was found that the wear resistance of carbon in WC particles in the coated file was weaker than that of tungsten. Thus, the carbon and tungsten in the filings were not present as tungsten carbide, even though the main XRD peaks detected in the coated file were WC (Figure 3). Although XRD and EDS analyses showed some  $\text{W}_2\text{C}$  was present after the file was coated with WC-12Co, using the thermal spray technique,<sup>23</sup> the  $\text{W}_2\text{C}$  peak could not be distinguished from WC in this XRD spectrum (Figure 3).

Finally, the conclusion was reached that the small amount of coating material abraded in the filings did not affect the determination of Cr content in the SRMs (Table 4). Moreover, the coated flat file was applied to obtain filings samples in the form of metal in the pressure vessels of fossil fuel, industrial, and nuclear power plants for the measurement of Cr content.

**Determination of Cr in the Outlet Header.** Samples were collected at four positions in the outlet headers. Each

**Figure 3.** XRD spectrum for the file coated with WC-12Co by HVOF.**Table 5.** Analytical results for the HRC in the disk form of SRMs, and for C and W in the filings of SRMs ground using a flat file coated with WC-12Co

SRM No	HRC <sup>a</sup>	C (%)			W ( $\mu\text{g g}^{-1}$ )		
		Certified	Found	Difference	Certified <sup>b</sup>	Found <sup>c</sup>	Difference
1269	11.3 ± 1.4	0.298	0.41	0.112	(10)	683 ± 73	673
1227	20.1 ± 1.8	0.97	1.03	0.06	30	903 ± 92	873
1226	23.8 ± 2.6	0.085	0.15	0.065	(50)	742 ± 76	692

<sup>a</sup>*n* = 5. <sup>b</sup>Values in parentheses are not certified and are given for information only. <sup>c</sup>*n* = 3.

**Table 6.** Analytical results for Cr contents in the filings collected from four outlet headers at nuclear power plants using a flat file coated with WC-12Co

Sample No	Cr (%) <sup>a</sup>	SD	RSD (%)
1-B <sup>b</sup>	0.113	0.003	2.7
1-M <sup>c</sup>	0.190	0.002	1.1
1-B <sup>b</sup>	0.119	0.003	2.5
2-B	0.114	0.001	0.88
2-M	0.112	0.002	1.8
2-B	0.112	0.004	3.6
3-B	0.111	0.002	1.8
3-M	0.125	0.003	2.4
3-B	0.126	0.001	0.79
4-B	0.111	0.004	3.6
4-M	0.174	0.003	1.7
4-B	0.165	0.008	4.8

<sup>a</sup>n = 3. <sup>b</sup>Branch line. <sup>c</sup>Main header body

outlet header consisted of one main header body and two branch lines. The outlet feeders were welded to nozzles that extruded from the header body and branch lines. Thus, the nozzles had the same chemical composition as the material from which they were pulled. Three samples were collected per outlet header position. One sample was collected from the thick-walled main header body, and two were collected from the thick-walled branch line. No sample was collected from the nozzles. As shown in Table 6, the Cr contents in the filings collected from the used outlet headers of the nuclear power plants were in the range of 0.11-0.19% using the flat file coated with WC-12Co. These results were not dependent on the outlet header or branch line positions. Because the chromium content in all samples was higher than 0.10%, the process of wall thinning in the pipe systems of outlet headers due to FAC would be expected to progress very slowly.

### Conclusions

This study established a sampling procedure for determination of chromium content in carbon steel pipe by ICP-AES. A flat file was used to obtain filings samples of the pipe systems made from carbon steel in nuclear power plants. A contamination problem, caused by a flat file made

of chrome steel, was solved by coating it with WC-12Co, using a HVOF spraying technique. After the disk-form of SRMs was ground with the coated flat file, analytical results for the Cr content in the filings of SRMs determined using ICP-AES were in good agreement with the certified values. Thus, the coated flat file can be applied to obtain filings samples of carbon steel in the pipe systems of fossil fuel, industrial, and nuclear power plants for the measurement of Cr content.

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