보건학석사 학위논문

Welding Filler Material Components for Reduction of Fume and Hexavalent Chromium Generation from Shielded Metal Arc Welding and Flux Cored Arc Welding

피복아크 및 플럭스 코어드 아크 용접에서 발생하는 흄 및 6가 크롬 발생 저감을 위한 용가재 성분 연구

2022년 8월

서울대학교 보건대학원
환경보건학과 환경보건학 전공
정 선 교

Welding Filler Material Components for Reduction of Fume and Hexavalent Chromium Generation from Shielded Metal Arc Welding and Flux Cored Arc Welding

피복아크 및 플럭스 코어드 아크 용접에서 발생하는 흄 및 6가 크롬 발생 저감을 위한 용가재 성분 연구

지도교수 윤 충 식

이 논문을 보건학석사 학위논문으로 제출함

2022년 5월

서울대학교 보건대학원
환경보건학과 환경보건학 전공
정 선 교

정선교의 보건학석사 학위논문을 인준함
2022년 6월

위 원 장	김 성 균	(인)
부위원장	이 기 영	(인)
위 원	윤 충 식	(인)

Abstract

Welding Filler Material Components for Reduction of Fume and Hexavalent Chromium Generation from Shielded Metal Arc Welding and Flux Cored Arc Welding

Sungyo Jung
Department of Environmental Health Sciences
Graduate School of Public Health
Seoul National University, Korea

Advisor Chungsik Yoon, Ph.D., CIH

Welding generates welding fumes and hexavalent chromium, which are classified as Group 1 carcinogens by the International Agency for Research on Cancer (IARC). In particular, due to the generation of high hexavalent chromium and fumes in shielded metal arc welding (SMAW) and flux-cored arc welding (FCAW), they impose a severe health risk upon exposure. Thus, this study aims to estimate the welding filler material components that can reduce the generation of fumes and hexavalent chromium in SMAW and FCAW.

In the current study, nine welding rods for SMAW and eight flux-cored wires for FCAW were tested. Each type of welding was performed under uniform conditions in a fume-hood. Collected fume samples were analyzed by gravimetric analysis to calculate fume generation rate (FGR) and ion chromatography with the ultraviolet detection (IC-UV) for hexavalent chromium generation rate (HCGR). Welding filler materials were analyzed using wavelength dispersive X-ray fluorescence

spectrometer (WDXRF). After performing statistical difference tests, a correlation analysis was conducted to estimate the statistical association between the generation rate and the content of filler component in the welding material in each type of welding. Based on the results of the correlation analysis, regression models were designed and then analyzed through multiple linear regression method. Finally, based on the results of correlation and multiple linear regression analyses, the component-combination formulas were designed and correlation analysis was conducted with fume generation rate and hexavalent chromium generation rate.

For nine SMAW welding rods, FGR(per welding time) was in the range of 198.0–289.3 mg/min, and HCGR(per welding time) was in the range of 5.34–7.98 mg/min. By changing the welding filler material components under the same welding conditions, the generation rate was found to be reduced by approximately 26.7% (AVG = 20%) and 24.8% (AVG = 3.4%) compared to base FGR and HCGR, respectively. In the case of eight flux-cored wires, FGR was 590.4–821.1 and HCGR was 0.34–3.31 mg/min, which could be reduced by up to 23.5% (AVG = 10%) and 89.7% (AVG = 47.1%), respectively, by changing the welding material components under the same welding conditions.

The results of correlation analysis of SMAW, with different elements as filler material, suggested a statistically significant correlation of fluorine (F), potassium (K), calcium (Ca), and sodium (Na) with FGR and chromium (Cr) and titanium (Ti) with HCGR. Whereas, in the case of FCAW, fluorine (F), potassium (K), and sodium (Na) with FGR and sodium (Na), potassium (K), silicon (Si), zirconium (Zr), and fluorine (F) with HCGR showed a statistically significant correlation.

In most multiple linear regression models, the multicollinearity problem arises due to the interference among independent variables. That is, some specific elements did not strongly contribute to the change in the value of the dependent variable, and several elements made complex contributions in the fume and hexavalent chromium

generation rate. So, this study proposed eleven component-combination formulas showing statistically significant correlation with dependent variables for SMAW and ten for FCAW.

This study suggests that it is possible to reduce FGR and HCGR without affecting the performance of welding by using different components as welding materials. In order to reduce HCGR, it is recommended to reduce the FGR for SMAW and to reduce the content of hexavalent chromium in welding fumes for FCAW. Also, it is recommended to manufacture welding materials with components that can suppress oxidation of chromium and have higher electronegativity than metal chromium and chromium compounds. Thus, by considering the oxidation ability and electronegativity of the compound, HCGR can be reduced.

If welding materials with low FGR and HCGR are manufactured and widely used in the field as per the suggested change in element content presented in this study, the problem of exposure to Group 1 carcinogens is expected to be fundamentally reduced.

Keyword : Welding Fume, Hexavalent Chromium, Correlation Analysis, Shielded Metal Arc Welding, Flux Cored Arc Welding

Student Number : 2020-29645

Table of Contents

Abstract i

1. Introduction 1

2. Materials and Methods 4

2.1. Study Subject 4

2.1.1. Welding Filler Material 4

2.1.2. Evaluation Condition 7

2.1.3. Study Procedure 9

2.2. Fume & Hexavalent Chromium Generation Rate Test 11

2.2.1. Sampling Strategy 11

2.2.2. Gravimetric Analysis 12

2.2.3. Hexavalent Chromium Analysis 13

2.2.4. Estimation of the Generation Rate 14

2.3. Composition Analysis of Welding Filler Material 15

2.3.1. Sampling Strategy 15

2.3.2. Instrumental Analysis 16

2.4. Statistical Analysis 17

3. Results 19

3.1. Fume Generation Rate 19

3.2. Hexavalent Chromium Generation Rate 22

3.3. Chemical Composition of Welding Filler Material 26

3.4. Correlation Analysis of Each Component 29

3.5. Multiple Linear Regression Analysis 30

3.6. Correlation Analysis by Proposed Formula 32

4. Discussion.. 35

5. Conclusions 40

6. References 41

Supplementary Materials 45

Abstract in Korean 60

List of Tables

Table 1. Welding conditions for different welding types used in this study. 6

Table 2. Comprehensive information for chemical composition analysis of welding material. １６

Table 3. Results of fume generation test and hexavalent chromium content in welding fume of welding rods and flux-cored wires in uniform welding conditions for different welding types. ２１

Table 4. Hexavalent chromium generation rate of each welding material in controlled welding condition for different welding types. ２３

Table 5. Results of multiple linear regression analysis using elements analysis result of flux in flux-cored wires for FCAW. ３１

Table 6. Pearson's correlation coefficients by each formula with per dependent variable using analysis result of element in welding filler materials in welding rods(for SMAW) and flux-cored wires(for FCAW). ３４

List of Figures

Figure 1. Structure of fume hood used in this study................................ 8

Figure 2. Schematic of the evaluation and analysis process used in this study... 10

Figure 3. Results of fume generation rate per welding time, hexavalent chromium generation rate per welding time and hexavalent chromium content in welding fume by each of nine welding rods used in this study. (FGR = Fume generation rate, HCGR = Hexavalent chromium generation rate, WT = Welding time) 24

Figure 4. Results of fume generation rate per welding time, hexavalent chromium generation rate per welding time and hexavalent chromium content in welding fume by each of eight flux-cored wires used in this study. (FGR = Fume generation rate, HCGR = Hexavalent chromium generation rate, WT = Welding time) 25

Figure 5. Graph presented analysis results of content (%) of each element in welding filler materials in welding rods for SMAW........................ 27

Figure 6. Graph presented analysis results of content (%) of each element in flux in flux-cored wires for FCAW 28

List of Supplementary Materials

Table S 1. Analytical condition and parameter for hexavalent chromium analysis by IC-UV. 46

Table S 2. Analytical condition and parameter for oxides components and elements analysis by XRF. 46

Table S 3. Fume generation test result of each welding material in controlled welding condition for different welding types. (AM±SD). 47

Table S 4. Mechanical Property of weld metal by AWS A5.4 E308-16 standard for STS-308 welding rod. 48

Table S 5. Mechanical Property of weld metal by AWS A5.22 E308LT0-1/4 standard for STS-308L welding wire. 48

Table S 6. Chemical components contents of oxides and elements in welding filler material in welding rods for SMAW. 49

Table S 7. Chemical components contents of oxides and elements in flux in flux-cored wires for FCAW. 51

Table S 8. Pearson's correlation coefficient by each parameter in welding filler materials of nine welding rods for SMAW. 53

Table S 9. Pearson's correlation coefficient by each parameter in flux of eight flux-cored wires for FCAW. 54

Table S 10. Results of multiple linear regression analysis using elements analysis result of welding filler materials in welding rods for SMAW. 55

Table S 11. Results of multiple linear regression analysis using oxides components analysis result of welding filler materials in welding rods for SMAW. 56

Table S 12. Results of multiple linear regression analysis using oxides components analysis result of flux in flux-cored wires for FCAW. 57

Table S 13. Pearson's correlation coefficients by each formula with per dependent variable using analysis result of oxides components in welding filler materials in welding rods (for SMAW) and flux-cored wires (for FCAW). 58

Table S 14. Reproducibility test result of hexavalent chromium content analysis in welding fume by filter type used for sampling welding fume. 59

Figure S 1. Process diagram of welding in fume hood for evaluating fume generation rate and hexavalent chromium generation rate in this study. 45

Figure S 2. Graph presented analysis results of content (%) of each oxide in welding filler materials in welding rods for SMAW. 50

Figure S 3. Graph presented analysis results of content (%) of each oxide in flux in flux-cored wires for FCAW. 52

1. Introduction

Welding is the process of bonding two or more materials together by applying energy. This work is mainly carried out by melting two metals together by the application of heat energy. It is widely used in Korea as well as around the world. It has been designated one of the six root industries designated by the Korean government. According to previous reports, the size of the welding equipment, accessories, and consumables market is on the rise and is expected to continue to increase over the next five years.

The type of welding varies depending on the purpose of use, arc generation method, protective gas presence, welding material type, etc. (K. Weman. (2012)). Welding is typically classified as gas welding, resistance welding, arc welding, newer welding, and solid state welding. Among them, arc welding is the most widely used in the field. According to the result of a survey on the use of welding materials in welding sites around the world, shielded metal arc welding (SMAW), mixed inert gas (MIG) welding, and flux-cored arc welding (FCAW) are known to be the most frequent in the field. In particular, SMAW does not need protective gas, uses a consumable welding rod and is frequently used in the field because of its simple equipment. FCAW is widely used due to its high welding speed, good appearance, and formation of deposited metal.

Welding changes the physical state of the metal through application of strong energy, it may have direct or indirect adverse health effects on welding workers and surrounding workers. According to previous studies, approximately 11 million workers worldwide are likely to be exposed to welding fumes during working hours; including temporary and accidental cases, 10 times the number of workers are likely to be exposed to welding fume (Ashley., et al. 2021).

Welding fumes are designated as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC) (2017); they are generally composed of harmful heavy metal components such as chromium (Cr), nickel (Ni), zinc (Zn), iron (Fe), manganese (Mn), copper (Cu), etc. Also, previous studies have shown that fumes generated by physical scattering and state change of metal particles during welding are highly harmful to health due to their physical characteristics such as respiratory sediments (mass median aerodynamic diameter < 1um) (Antonini., et al. 2008; Ennan., et al. 2013; Vishnyakov., et al. 2013). Among them, hexavalent chromium, which occurs during welding, is also an IARC-designated Group 1 carcinogen. It is mainly inhaled through the respiratory tract and is highly toxic, which can cause serious adverse health effects even when exposed for a short period of time.

The mechanism of the generation of welding fume was suggested in a study by Hewitt and Hirst (1993). The generation rate of welding fumes has been known to be affected by welding type (SMAW, FCAW, etc.), welding material (welding rods, flux-cored wires, etc.), welding conditions (current, voltage, contact tip to work piece distance (CTWD), type and concentration of shield gas), base material, and environmental factors (temperature, relative humidity), etc. It has been reported that, among the many welding types, the highest amount of welding fumes are generated in FCAW and SMAW (Palmer and Eaton, 1994; Palmer., 1983). According to a previous study (Yoon., 1999; Yoon., et al. 2003), the rate of welding fume generation per welding time changes as per the welding conditions, such as welding current and welding voltage, in flux-cored arc welding. FGR per welding time increases as welding current and input power (by the current and voltage) increase in a statistically significant way. It was suggested that more than 85% of the welding fumes were derived from welding material (Voitkevich., 1995). In particular, heavy metals in welding fumes were mainly derived from welding material (Palmer and Eaton, 1994; Palmer., 1983).

The formation mechanism of hexavalent chromium, which is a carcinogen and highly toxic to humans, in SMAW was suggested in a study by Koppen., et al. (1981). In addition, the concentration and solubility of the components in welding fumes were found to be influenced by the welding conditions and the welding filler materials (Floros., 2018; McCarrick., et al. 2019; Mei., et al. 2018). In the case of FCAW, a statistically strong association between fluorine (F), often containing sodium (Na) or potassium (K), and soluble hexavalent chromium was suggested in previous studies (Mei., et al. 2018; Tandon., et al. 1985; Floros., 2016).

As suggested previously, welding fume and hexavalent chromium generation during welding is largely determined by welding types, welding conditions, and the components in welding filler materials. However, studies on the roles of welding filler material components in welding fume and hexavalent chromium generation have been relatively few. Additionally, it has been confirmed that low welding current and input energy can reduce welding fume generation per welding time (Yoon., 1999). However, the most important thing in welding is the performance, characterized by good welding bead formation, welding quality, welding efficiency, welding speed, tensile strength, and elongation. If conditions such as welding current and input energy are altered to reduce welding fume, the performance may be compromise due to the influence of arc forming energy. Also, in some cases, it is difficult to control the welding conditions at the work site. Therefore, in order to ensure welding performance and reduce the generation of welding fume and hexavalent chromium, it would be necessary to adjust the components of the welding filler material as they contribute to 85% or more in composition of welding fume. Thus, this study aims to reduce welding fume and hexavalent chromium generation by controlling the components of welding filler material and flux, which form slag and protect arc formation and molten metal. As suggested in previous studies, the type of welding is a major variable affecting the generation and composition of welding fume, so the results of this study were divided according to the type of welding (SMAW and FCAW).

Accordingly, this study aims to provide scientific evidence for the reduction of fume and hexavalent chromium generation by estimating the components of welding filler material, which plays a vital role in controlled welding conditions. Therefore, through this study, fundamental solutions are suggested that can control the hazardous carcinogen exposure problem of workers exposed to welding fumes. In particular, this study focused on SMAW with a large amount of hexavalent chromium generation and FCAW with a large amount of fume generation per welding time.

2. Materials and Methods

2.1. Study Subject

2.1.1. Welding Filler Material

SMAW was performed on nine types of consumable stainless-steel welding rods (SS-308) that had 18% Cr and 8% Ni, which were designed to prevent oxidation of chromium and meet the AWS A5.4-06 (E308-16) standards. Of the nine rods used in this study, seven (one base product and six test products) were manufactured by the same manufacturer by adjusting components of welding filler materials for reduced welding fume and hexavalent chromium generation. The other two welding rods were procured from different manufacturers for comparison.

For FCAW, eight types of flux-cored wires (FCW) that meet the AWS A5.22 E308LT0-1/4 standard were used. The wires consisted of a low carbon material with 18% Cr and 8% Ni steel (SS-308L), which can prevent oxidation of chromium. The FCW used in this study were obtained from the same manufacturer, including one base product and seven test products, customized by adjusting only components in flux for reduced welding fume and hexavalent chromium generation.

Welding rods and FCW used in this study were pre-tested to guarantee melting efficiency of deposited metal and the appearance of welding bead formation by experts. Regarding products that were manufactured by altering the alloys except the alkali and fluoride components of the material, the welding performance was evaluated by analyzing the physical properties and performance of the welding metal. In the case of FCW, it was difficult to collect flux inside the wires for various manufacturers, so they were excluded from the comparative study.

The welding rods for SMAW were manufactured with different chemical components of core-wire and filler material. The FCW for FCAW was manufactured with different components of flux filled inside the wire. In the case of hoop and base metals used for welding in this study, the same material is used for unification of the welding condition.

The welding conditions for the nine welding rods for SMAW and the eight FCW for FCAW were as recommended by the manufacturer, and unified by welding type. To obtain accurate results, uniform welding conditions were maintained for each type of welding. The confounder effect generated due to the difference in the amount of welding fumes and hexavalent chromium in different welding conditions was controlled. The welding conditions were standardized as recommended by the manufacturer to achieve the optimal welding performance of the welding rods and FCW in terms of the alloy material, diameter of welding materials, welding posture, etc. The welding conditions were customized by welding type and its characteristics, such as equipment used during welding and whether or not a shield gas was used. Thus, the difference in the abovementioned conditions may affect the amount of fume and hexavalent chromium generated. Therefore, the results of fume and hexavalent chromium generated during welding were classified and statistically analyzed by type of welding. Controlled welding conditions for different welding types are shown in Table 1.

Table 1. Welding conditions for different welding types used in this study

Type	Class	AWS	Product	Welding Posture	Welding Time (S)	Diameter (mm)	Current (A)	Voltage (V)	Temperature (˚C)	Relative Humidity (%)	Speed (cm/min)	CTWD (mm)	Gas(CO_2) Flow (L/min)
SMAW	SS-308	AWS A5.4-06 (E308-16)	9	All	60	3.2	110	24	22.4	38	-	-	-
FCAW	SS-308L	AWS A5.22 (E308LT0-1/4)	8	Flat (7) All (1)	30	1.2	200	30	22.4	38	35	20	25

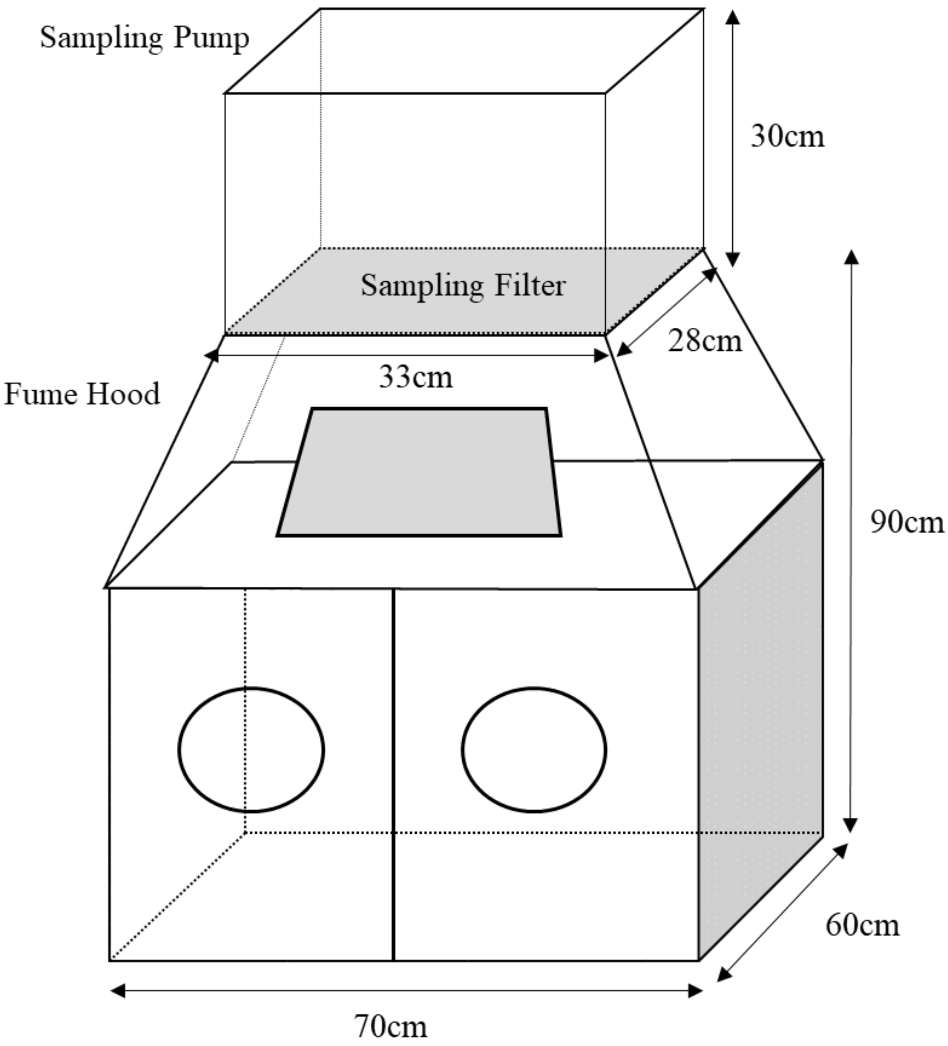
2.1.2. Evaluation Condition

In this study, the evaluation of fume generation rate (FGR) and hexavalent chromium generation rate (HCGR) were performed according to 1SO 15011-4 and KS D 0062 standards. For evaluation, welding and fume sampling were performed in the fume hood manufactured according to standards. The structure of the fume hood used is shown in Figure 1, and the evaluation diagram of FGR and HCGR is shown in Figure S1. Every test was conducted after removing airborne particles using an air pressure gun.

The fume hood had an openable window in the front with holes to facilitate ease of use. through. On the upper side, there was a translucent plastic window so that the welder could check the formation and stability of arc during welding. Since the top of the fume hood was openable, sampling filler (254 mm x 203 mm) of sampling pump could be attached to the hood. Sampling was conducted at a flow rate of 1.5~2.3 m^3/min.

First, the base metals that were at least 14 mm and a size of 260 mm x 260 mm were selected, according to the KS D 3503 (SS400) and KS D 3515 (SM400B) standards. But, in this study, SS-304L alloy base metal for SMAW and stainless-steel (SS) hoop for FCAW were used.

Figure 1. Structure of fume hood used in this study.



2.1.3. Study Procedure

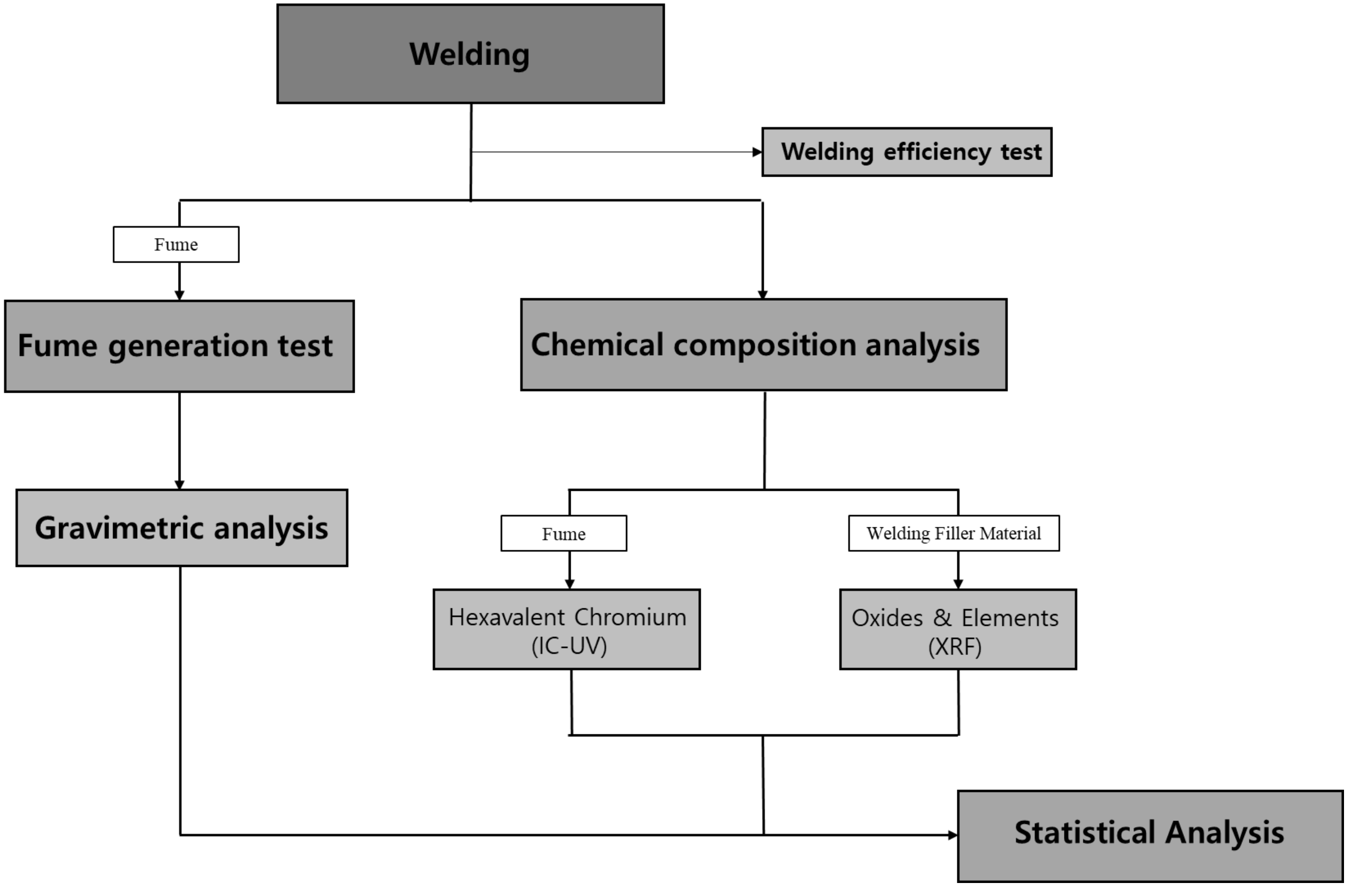
The procedure followed in this study is presented in Figure 2. First, the welding bead formation state was evaluated by the experts, and then the welding efficiency was evaluated based on welding materials manufactured with different chemical components. Welded products with no defects were examined for physical strength, while products with any defects were detected in the pre-test and were excluded from the subsequent procedure.

Thereafter, the selected welding products were evaluated for FGR under unified welding conditions for different types of welding as per the standards. Then, hexavalent chromium was analyzed in the collected fumes to determine its share in the fume, and through this, the HCGR amount was calculated.

Next, for SMAW, the filler material of the welding rod was collected and analyzed. In the case of FCAW, the flux was collected and analyzed to determine the chemical composition of the welding material. Despite the fact that welding rods for SMAW had different core-wire, results of their chemical composition were similar to each other in pre-survey. Therefore, in this study, only filler material was collected and analyzed for the chemical components of the welding rods of SMAW.

The acquired data were used for statistical estimation using Pearson's correlation test, using FGR and HCGR as dependent variables and the content of each chemical component of welding material as independent variables. Finally, analysis of specific components or formulas showed an association of FGR and HCGR in SMAW of SS-308 class and FCAW of SS-308L class.

Figure 2. Schematic of the evaluation and analysis process used in this study



2.2. Fume & Hexavalent Chromium Generation Rate Test

2.2.1. Sampling Strategy

The evaluation of FGR was conducted as per ISO 15011-4 and KS D 0062. According to the KS M 0050 specification, a glass fiber filter (GFF) of size 254 mm x 203 mm was used for collecting welding fume samples during sampling time to determine FGR. The GFF used in this study was selected to have at least 99.9% filtration efficiency for particles of size 0.3 µm (GB-100R, ADVANTEC, Toyo Roshi Kaisha, Ltd.). Welding was performed as described in sections 2.1.2 and 2.1.3 of this manuscript, and the welding fume were collected at a flow rate of 2.0 m^3/min using a pump with a GFF attached to the upper end of the hood.

To determine HCGR, fumes were collected using a customized filter made of PTFE-D (Polytetrafluoroethylene, Hydrophobic) of the same size as that of the GFF, with a pore size of 0.20 µm (HYUNDAI MicroCo., Ltd.). To evaluate the HCGR, the content (%) of hexavalent chromium in fumes was analyzed. In the process of collecting fumes using a GFF filter and aliquoting it for analysis, glass fibers on the surface of the GFF filter and silicon oxide components were collected as impurities. It was observed that due to the non-uniform collection phenomenon, the standard deviation between derived samples was high. When the hexavalent chromium content analysis of the collected fume by GFF in pre-test, It was assessed that either silicon oxide components, not fumes, were collected and that affected the calculation of fume mass, or that silicon oxide components were collected together with fumes to affect the chemical stability and composition of hexavalent chromium in the fume. Therefore, in this study, while evaluating HCGR, welding fumes were collected in custom made hydrophobic PTFE filter with low surface adsorption and chemical reaction to overcome the problems shown in pre-test. The collected fumes were separated into 15 mL conical tubes in 0.1~0.2 g using a spoon taped with Teflon and then weighed before and after aliquoting using an electronic balance with a least count of 1 mg. The results of the difference in precision when analyzing the hexavalent chromium content in fume according to the type of filter are presented in Figure S14.

For SMAW (n = 9), FGR (mg/min) was relatively lower than that of FCAW (n = 8). Thus, for SMAW, welding was conducted for 60 s, whereas for FCAW, welding duration was 30 s. In addition, welding fume was collected for 200 s from the beginning using a pump with filter paper in both SMAW and FCAW welding when evaluating the FGR and HCGR.

All tests were conducted thrice per product, and fume collection for the evaluation of HCGR was performed at least thrice per test.

2.2.2. Gravimetric Analysis

The GFF filter used for evaluating FGR was weighed with an electronic balance. The filter was dried for at least 3 h in a drying furnace at a temperature of about 100 °C before and after sampling to exclude the effect of moisture in the air. The collected welding fume was analyzed using weight before and after sampling and calculated according to Equation (1) below.

$$Collected\ Welding\ Fume\ (mg) = W(post) - W(pre) \quad \text{Equation (1)}$$

W(post) = Weight of sample contained in filter after sampling (mg)

W(pre) = Weight of filter before sampling (mg)

In addition, the weight of the base metal was measured before and after welding to calculate the weight of the deposited metal through welding. The weight of the welding material was measured before and after welding to calculate the usage of welding material. Both base metal and welding materials were measured with an electronic balance and were calculated according to Equations (2) and (3).

$$Amount\ of\ Deposited\ Metal\ (g) = W(post) - W(pre) \quad \text{Equation (2)}$$

W(post) = Weight of base metal after welding (g)

W(pre) = Weight of base metal before welding (g)

$$Welding\ Material\ Usage\ (g) = W(pre) - W(post) \quad \text{Equation (3)}$$

W(pre) = Weight of welding material before welding (g)

W(post) = Weight of welding material after welding (g)

Finally, in order to calculate the hexavalent chromium content (%) in the fume, the 15 mL conical tubes with fume were weighed on an electronic balance. The fume in the conical tube was analyzed by weighing before and after aliquoting, and calculated as per Equation (4) below.

$$Aliquoted\ Welding\ Fume\ (mg) = W(post) - W(pre) \quad \text{Equation (4)}$$

W(post) = Weight of conical tube after aliquoting welding (g)

W(pre) = Weight of conical tube before aliquoting welding (g)

2.2.3. Hexavalent Chromium Analysis

In this study, the hexavalent chromium content (%) of the collected fume was analyzed to calculate HCGR. When analyzing hexavalent chromium in welding fumes, the standards of ISO 16740 (2005) and NIOSH NMAM 7605 (2003) were referenced.

A total of 5 mL of 2% NaOH and 3% Na_2CO_3 extraction solution were prepared 24 h before evaluation and injected into a conical tube containing about 0.1~0.2 g of weighed welding fume. Then, they were purged with nitrogen gas for at least 3 min per sample. Since hexavalent chromium is chemically unstable and can be easily converted into trivalent chromium, which is relatively stable in air and general environments, the whole process of injection of extraction solution and nitrogen gas purging was performed within 10 min of welding fume collection (Yoon, 2003).

After that, the processed samples were stored and transported in a freezing condition. Pre-treatment and analysis were performed within 24 h of transportation to the laboratory. The collected fumes were analyzed through a heating pre-treatment process referring to the ISO 16740 specification. According to previous studies, since a large amount of chromium compound and other heavy metals are present in the fumes, trivalent chromium in the sample can be oxidized to hexavalent chromium during the heating pre-treatment, resulting in an over-evaluation of hexavalent chromium. Accordingly, in the pilot test, the repeatability and recovery of hexavalent chromium in the heating and sonication pre-treatment methods were tested on the matrix: (1) with other heavy metals such as Cr; and (2) with welding fume. From previous studies, the sonication pre-treatment method was proposed because of its better repeatability and recovery than heating pre-treatment (Yoon, 2003; Ashley, 2009). But, in the pilot test of this study, the repeatability and recovery of the heating pre-treatment method were found to be better than those of the sonication. So, pre-treatment for hexavalent chromium analysis was performed with the heating pre-treatment method according to ISO 16740.

First, the sample was heated on a hot plate at 100 °C for 40 min. After that, distilled water was injected to adjust the final volume to 50 mL, and then the sample was further diluted 100 times using distilled water. Finally, the sample was filtered with a syringe filter and analyzed by ion chromatography with the ultraviolet detection (IC-UV). Analytical conditions of IC-UV are shown in Table S1.

The analyzed hexavalent chromium concentration (μg/mL) was converted into μg/sample units through processing of limit of detection (LOD) values, blank sample correction, and recovery correction, and through Equation (5), the hexavalent chromium content (%) in fume was calculated.

$$Cr(6)\ in\ Welding\ Fume\ (\%) = \frac{Cr(6)\ (\mu g/sample)/10^6}{Aliquoted\ Welding\ Fume\ (g)} \times 100 \quad \text{Equation (5)}$$

2.2.4. Estimation of the Generation Rate

In the case of the FGR, three types of fume generation rates depending upon welding time (Eq (6)), weight of deposited metal (Eq (7)) and material usage (Eq (8)) were calculated, where the weight of the welding fume collected on GFF was calculated from Equation (1)

$$FGR\ per\ Welding\ Time\ (mg/min)\ = \frac{Collected\ Welding\ Fume\ (mg)}{Welding\ Time\ (min)}$$ Equation (6)

$$FGR\ per\ Deposited\ Metal\ (mg/g)\ = \frac{Collected\ Welding\ Fume\ (mg)}{Deposited\ Metal\ (g)}$$ Equation (7)

$$FGR\ per\ Material\ Usage\ (mg/g)\ = \frac{Collected\ Welding\ Fume\ (mg)}{Material\ Usage\ (g)}$$ Equation (8)

In addition, based on the calculated FGR, the amount of HCGR was calculated according to Equation (9), where hexavalent chromium content in welding fume was calculated from Equation (5).

$$HCGR = \ FGR\ \ \times Cr(6)\ in\ Welding\ Fume(\%)$$ Equation (9)

2.3. Composition Analysis of Welding Filler Material

2.3.1. Sampling Strategy

The welding rod used in SMAW was ruptured to collect filler material attached to the surface of welding rod. Thereafter, the filler material was powdered with a grinder, and aliquoted in a conical tube using a Teflon-taped spoon.

In the case of FCW used in FCAW welding, only flux was collected because the core wire and hoop used in this study were the same and only the flux components filled therein were different. All the wires used in this study were from same manufacturer, and the flux raw material was provided in the form of powder and aliquoted to the conical tube using a Teflon-taped spoon.

All the samples collected were weighed with an electronic balance before and after the powder was aliquoted. The collected welding material was analyzed using Equation (10).

$$Collected\ Welding\ Material\ (mg) = W(post) - W(pre) \quad \text{Equation (10)}$$

W(post) = Weight of conical tube after aliquoting sample (g)

W(pre) = Weight of conical tube before aliquoting sample (g)

2.3.2. Instrumental Analysis

In order to characterize the chemical composition of the collected welding materials XRF was conducted. The data regarding the components investigated, pre-treatment methods, and reference specifications for XRF analysis are listed in Table 2.

Table 2. Comprehensive information for chemical composition analysis of welding material.

Category	Target	Reference	Sample preparation	Equipment
Oxides	SiO_2, TiO_2, K_2O, Na_2O, Nb_2O_5, P_2O_5, SO_3, MoO_3, Bi_2O_3, ZrO_2, Etc.	**[KS M 0017, KS D 1654, KS E ISO 9516]**	**Compressing** samples at 25 ton atm for 1 min.	**X-Ray Fluorescence (WDXRF)** (S8-Tiger(Series 1)., Bruker AXS)
Elements	Si, Ti, K, Na, F, Fe, Cr, Mo, Nb, Etc.			

Sample pre-treatment was conducted according to the press pallet method. First, 1.5 g of organic material that would not affect XRF analysis was applied to the pallet. Then, 0.5 g of the welding material sample was applied uniformly to the pallet. Thereafter, a pallet made of aluminum mounted on a press holder, compressed with a pressure of 25 t for 1 min, and pre-treated into a cylindrical solid having a diameter of 34 mm.

To analyze oxides and elements in welding material, each sample was observed thrice in XRF in vacuum. A repeatability test was conducted by analyzing each sample more than three times. Also, the authenticity of elements analyzed through small peaks and overlapped regions were checked. Finally, a normalization process was performed, where samples were analyzed twice in XRF. First, the element content of sample was analyzed, and then the oxide compound contained in the sample was analyzed. Additionally, the oxide content observed from the XRF analysis does not represent the true composition owing to the characteristics of the XRF device. Briefly, the oxide derived from the analysis may not be present in the sample in the exact form, but may be present in another form. The detailed analytical conditions are presented in Table S2.

2.4. Statistical Analysis

The data calculated through measurement and analysis were presented using descriptive statistics. The FGR and HCGR of welding materials were presented using the arithmetic mean (AM) and standard deviation (SD). In addition, the results of the hexavalent chromium content (%) in the fume and the component content of welding material were also presented using the AM and SD. In this study, all the evaluations of measuring and analyzing were conducted at least thrice per sample, and statistical tests were conducted for the replicates.

Thereafter, the rate of change (%) of FGR, hexavalent chromium content in welding fume, and HCGR for each sample was calculated and compared to the base welding rod and wire set as controls in SMAW and FCAW. The values obtained during welding from each rod and wire were tested for statistically significant differences with the values of base rod and wire through a two-sample T-test after normality test. Therefore, it was examined whether there was a significant difference in the FGR and HCGR of welding rods and wires manufactured specifically to produce a lower amount of fume and hexavalent chromium compared to the base products. The chemical component content of the welding filler material in the welding rod and the flux in the wire was also compared with corresponding base materials for statistically significant difference. The statistical difference test results were presented as p-values, and statistical significance was set to $p<0.05$.

Among the data, the FGR and HCGR were set as dependent variables, and the resultant components of each welding material were set as independent variables. A Pearson's correlation test was conducted to estimate the statistical association between fume or hexavalent chromium generation and the component content of each welding material. For correlation analysis, a normality test was performed for each independent variable and dependent variable. Subsequently, Pearson's correlation analysis was performed when the variables followed normality, and the Pearson's correlation coefficient r value was presented as a result. Among the results, the relationship between the welding materials with at least 0.01% content and correlation coefficient of $r>0.6$ was classified as correlated, and the statistical significance was set at $p<0.05$.

Next, multiple linear regression analysis was performed on components that showed correlation with the FGR and HCGR. The components that were set as independent variables in multiple linear regression model were, β −coefficient, SE, standardized β −coefficient, and p-value. Independent variables were calculated for the estimation of the contribution and statistical significance of each dependent variable. Based on this, independent variables with statistically significant results were selected for the final regression model, and the variance inflation factor (VIF) index of the variables was calculated to examine the interference effect between the independent variables. Next, the suitability of the regression model was evaluated by calculating F-statistics, adjusted R^2, and p-value. In this process, the multicollinearity evaluation criterion was set to $VIF<10$ and statistical significance was set to $p<0.05$. A total of nine welding rods and eight flux-cored wires were tested in this study. Since the number of samples used for multiple regression analysis was small and there were some components in welding filler material that showed a strong correlation with others, the covariance of the regression model was very large. Most of the multiple regression analysis results were not suitable for statistically analyzing and interpreting the results performed in this study.

Finally, based on the results of the correlation analysis and multiple linear regression analysis, formulae were compiled for the components that showed statistically significant association with the dependent variables. After the values were derived from the corresponding formula for each welding material, the statistical correlation between the FGR and HCGR was tested through correlation analysis with the dependent variable. For the correlation analysis, Pearson's correlation analysis was performed after the normality test, and the value of Pearson's correlation coefficient r was presented for each analysis result.

3. Results

3.1. Fume Generation Rate

The results of evaluation of the fume generation rate based on the use of welding materials under uniform welding conditions for different welding types are shown in Table S3. All evaluations were performed at least three times, and the data in the table were presented in the form of arithmetic mean (AM) ± standard deviation (SD) by the results of each evaluation. Evaluation results are listed in Table 3 and Table S3.

In the case of SMAW, it was confirmed that the amount of fume generated per welding time was significantly reduced in the six welding rods, excluding two welding rod products. Fume generation rate per welding time was 198.0–289.3 mg/min (AVG = 237.8 mg/min). It was verified that the fume generation rate per welding time of welding rod products manufactured with different welding filler material components could be reduced to the generation rate corresponding to 73.3% (AVG = 80%) of the base welding rod product. In addition, the welding efficiency of deposited metal among welding rods was more than 60% in all eight products except for one, and the value of the product also showed an efficiency of 59.7%. Therefore, it was observed that there was no significant performance difference in terms of welding efficiency of deposited metal for different welding material components.

For FCAW, the fume generation rate per welding time among eight flux-cored wires was 590.4–821.1 mg/min (AVG = 699.0 mg/min), and the minimum value was about 71.9% of the maximum value. Further, five flux-cored wires out of a total of seven tested wires showed a significant reduction in fume generation rate per welding time than the base product. It was confirmed that the fume generation rate could be reduced by up to 76.5% (AVG = 90%) compared to the base product depending on the change in flux components among the flux-cored wires. Additionally, in the case of welding type of FCAW, as derived by its welding characteristics, all eight flux-cored wires showed a welding efficiency of deposited metal of more than 80%, which was relatively higher than that of SMAW. However, as shown in the SMAW results, it was confirmed that no significant performance difference was observed when welding was performed with different flux-cored wires composed of different flux components in terms of the welding efficiency of deposited metal.

The data obtained by evaluating the mechanical properties of metals welded by welding rods, which were manufactured with different alloy components in filler material among SMAW products, are shown in Table S4. Since all the welding rods were classified in SS-308 alloy standard, the evaluation was conducted in accordance with AWS A5.4E308-16 standard. Tests were performed on eight welding rods out of nine rods. The welding performance of tested welding rods with different alloy components of filler material showed that they did not have defects, which was verified by results of tensile strength (MPa, >550) and elongation (%, >30%) of all welded metal above the standard value.

In the case of FCAW, four products were manufactured using different alloy components, and the mechanical properties of the welded metal using these flux-cored wires are as shown in Table S5. As all of these wires were classified in SS-308L alloy standard, the evaluation was conducted according to the AWS A5.22 E308LT0-1/4 standard. Tests were performed on four flux-cored wires out of nine products. Also, it was confirmed that the welding performance among tested wires was not significantly changed, with results of the tensile strength (MPa, >550) and elongation (%, >30%) above the standard value.

Notably, when welding is conducted under unified welding conditions for each welding type, it was observed that the amount of fume generated in most welding rods and flux-cored wires could be significantly reduced by changing the chemical composition of the welding filler material.

Table 3. Results of fume generation test and hexavalent chromium content in welding fume of welding rods and flux-cored wires in uniform welding conditions for different welding types.

Type	Product	Cr(6) content in Fume			Fume Generation Rate per								
					Deposited Metal			Welding Time			Material Usage		
		%	p-value	Change rate (%)	mg/g	p-value	Change rate (%)	mg/min	p-value	Change rate (%)	mg/g	p-value	Change rate (%)
SMAW (n=9)	S-A	2.45 ± 0.30	Standard		15.4 ± 1.3	Standard		289.3 ± 18.0	Standard		10.0 ± 1.2	Standard	
	S-B	2.36 ± 0.15	0.67	96.1	14.2 ± 1.7	0.39	92.0	285.3 ± 35.9	0.87	98.6	9.6 ± 1.3	0.72	96.5
	S-C	2.52 ± 0.11	0.73	102.7	10.7 ± 0.5	<0.05	69.7	212.0 ± 12.0	<0.01	73.3	6.8 ± 0.4	<0.05	68.5
	S-A1	3.71 ± 1.49	0.28	151.2	11.0 ± 1.1	<0.05	71.3	198.0 ± 25.5	<0.01	68.4	7.1 ± 0.6	<0.05	71.0
	S-A2	3.00 ± 0.18	0.07	122.3	12.2 ± 0.9	<0.05	79.0	222.7 ± 19.7	<0.05	77.0	7.8 ± 0.6	0.07	78.0
	S-A3	3.16 ± 0.32	<0.05	129.0	11.6 ± 1.1	<0.05	75.3	222.0 ± 8.5	<0.05	76.7	7.3 ± 1.1	<0.05	73.5
	S-A4	2.84 ± 0.14	0.14	115.9	12.4 ± 1.2	<0.05	80.5	226.7 ± 20.5	<0.05	78.4	7.9 ± 0.7	0.07	79.1
	S-A5	3.13 ± 0.16	<0.05	127.8	12.7 ± 1.1	0.05	82.1	254.7 ± 22.7	0.11	88.0	7.6 ± 0.6	0.05	75.9
	S-A6	3.18 ± 0.27	<0.05	129.6	11.8 ± 1.2	<0.05	76.4	229.3 ± 23.4	<0.05	79.3	8.1 ± 0.6	0.09	81.8
FCAW (n=8)	F-A	0.43 ± 0.02	Standard		12.3 ± 0.4	Standard		772.1 ± 20.0	Standard		10.8 ± 0.4	Standard	
	*F-A1	0.17 ± 0.02	<0.01	40.6	8.9 ± 0.1	<0.01	72.0	687.4 ± 22.9	<0.01	89.0	7.1 ± 0.1	<0.01	85.6
	F-A2	0.29 ± 0.02	<0.01	67.9	8.0 ± 0.2	<0.01	64.6	590.4 ± 6.5	<0.01	76.5	7.0 ± 0.2	<0.01	69.1
	F-A3	0.35 ± 0.16	0.48	80.6	8.5 ± 0.1	<0.01	69.2	639.4 ± 4.0	<0.01	82.8	7.5 ± 0.2	<0.01	79.4
	F-A4	0.24 ± 0.04	<0.01	55.2	10.9 ± 1.2	0.13	88.7	821.1 ± 91.9	0.45	106.4	9.4 ± 1.0	0.07	93.4
	F-A5	0.26 ± 0.01	<0.01	60.2	10.6 ± 0.2	<0.01	85.9	796.6 ± 52.6	0.49	103.2	9.3 ± 0.6	<0.05	90.0
	F-A6	0.45 ± 0.01	0.22	105.2	9.3 ± 0.3	<0.01	75.4	616.6 ± 17.5	<0.01	79.9	8.2 ± 0.4	<0.01	76.0
	F-A7	0.05 ± 0.01	<0.01	11.7	10.0 ± 0.6	<0.01	81.3	668.0 ± 7.1	<0.01	86.5	8.7 ± 0.3	<0.01	75.9

* P-value : results of independent two-sample T-test
* Change rate(%) : (value of product / value of base product) x 100

3.2. Hexavalent Chromium Generation Rate

The values of hexavalent chromium content in welding fume and hexavalent chromium generation rate under uniform welding conditions for different welding type and welding materials are shown in Table 3 and Table 4. Hexavalent chromium content (%) in welding fume(Figure S3) was derived from the results of analysis for at least three aliquoted welding fume per each welding materials. In addition, the hexavalent chromium generation rate was calculated by multiplying the average value of the hexavalent chromium content (%) in welding fume with the average value of the fume generation rate by welding materials according to Equation 9.

In the case of SMAW, only three welding rods showed significantly different results than the base welding rod in hexavalent chromium content in welding fume. Moreover, it was confirmed that most of the tested welding rods showed higher hexavalent chromium content in the welding fume than the base welding rod. However, the hexavalent chromium generation rate among welding rods could be reduced due to the effect of the reducing fume generation rate. The amount of hexavalent chromium generated per welding time could be reduced by up to 75.2% (AVG = 96.6%) of base welding rod. In addition, hexavalent chromium generation rate per welding time was 5.34–7.98 mg/min (AVG = 6.9 mg/min) among welding rods. By using different welding rods made by different welding filler material, hexavalent chromium generation rate per welding time could be changed to 66.9% than maximum value. It was estimated that this is due to the reduction of fume generation rate rather than the hexavalent chromium content among fume.

For FCAW, it was confirmed that the content of hexavalent chromium in the welding fume was significantly reduced in five wires. In particular, the test results showed that the value of hexavalent chromium content in flux-cored wires was lower than the base wire by up to 11.7% (AVG=60.2%) in welding fume generated by welding. Moreover, the hexavalent chromium generation rate per welding time was reduced up to 10.3%(AVG=47.1%) in all test wires compared to the base wire. It was estimated that the reduction of hexavalent chromium content in welding fume strongly contributed to the reduction of the hexavalent chromium generation rate.

Figure 3 shows the results of the fume generation rate per welding time, hexavalent chromium generation rate per welding time, and the hexavalent chromium content in welding fume of nine welding rods tested in this study. The results of eight flux-cored wires tested in this study are shown in Figure 4.

Table 4. Hexavalent chromium generation rate of each welding material in controlled welding condition for different welding types. (AM±SD).

Type	Product	Welding Time (S)	Sampling Time (S)	Cr(6) in Fume (%)	Hexavalent Chromium Generation Rate					
					Deposited Metal (mg/g)	Change rate (%)	Welding Time (mg/min)	Change rate (%)	Material Usage (mg/g)	Change rate (%)
SMAW (n=9)	S-A	60	200	2.45 ± 0.30	0.38	Standard	7.1	Standard	0.24	Standard
	S-B			2.36 ± 0.15	0.33	86.8	6.73	94.8	0.23	95.8
	S-C			2.52 ± 0.11	0.27	71.1	5.34	75.2	0.17	70.8
	S-A1			3.71 ± 1.49	0.41	107.9	7.35	103.5	0.26	108.3
	S-A2			3.00 ± 0.18	0.37	97.4	6.68	94.1	0.23	95.8
	S-A3			3.16 ± 0.32	0.37	97.4	7.03	99.0	0.23	95.8
	S-A4			2.84 ± 0.14	0.35	92.1	6.45	90.8	0.22	91.7
	S-A5			3.13 ± 0.16	0.4	105.3	7.98	112.4	0.24	100.0
	S-A6			3.18 ± 0.27	0.37	97.4	7.3	102.8	0.26	108.3
FCAW (n=8)	F-A	30	200	0.43 ± 0.02	0.05	Standard	3.31	Standard	0.046	Standard
	*F-A1			0.17 ± 0.02	0.02	40.0	1.2	36.3	0.012	26.1
	F-A2			0.29 ± 0.02	0.02	40.0	1.72	52.0	0.02	43.5
	F-A3			0.35 ± 0.16	0.03	60.0	2.21	66.8	0.026	56.5
	F-A4			0.24 ± 0.04	0.03	60.0	1.94	58.6	0.022	47.8
	F-A5			0.26 ± 0.01	0.03	60.0	2.06	62.2	0.024	52.2
	F-A6			0.45 ± 0.01	0.04	80.0	2.78	84.0	0.037	80.4
	F-A7			0.05 ± 0.01	0.01	20.0	0.34	10.3	0.004	8.7

* Change rate(%) : (value of product / value of base product) x 100

Figure 3. Results of fume generation rate per welding time, hexavalent chromium generation rate per welding time and hexavalent chromium content in welding fume by each of nine welding rods used in this study. (FGR = Fume generation rate, HCGR = Hexavalent chromium generation rate, WT = Welding time)

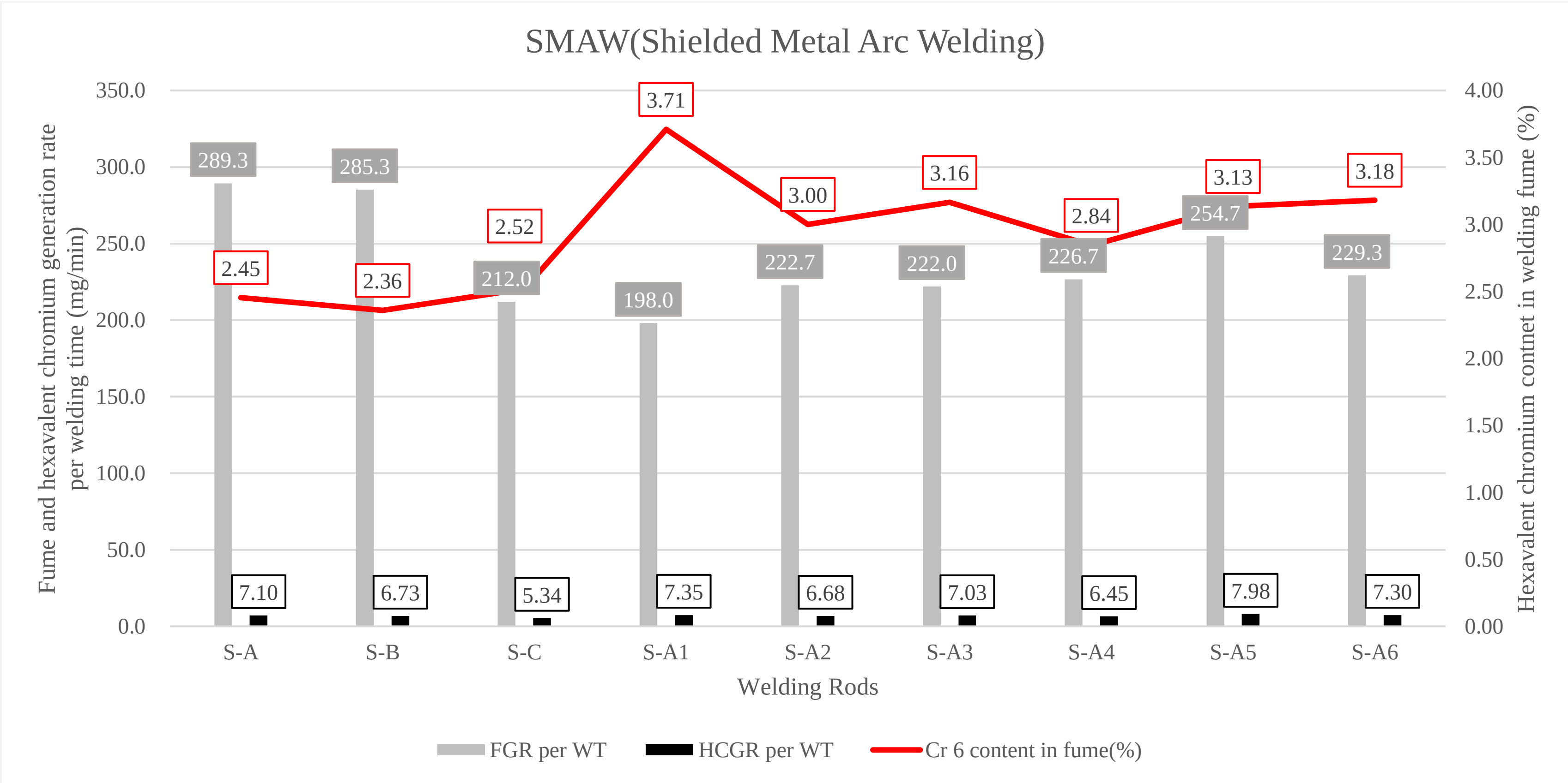
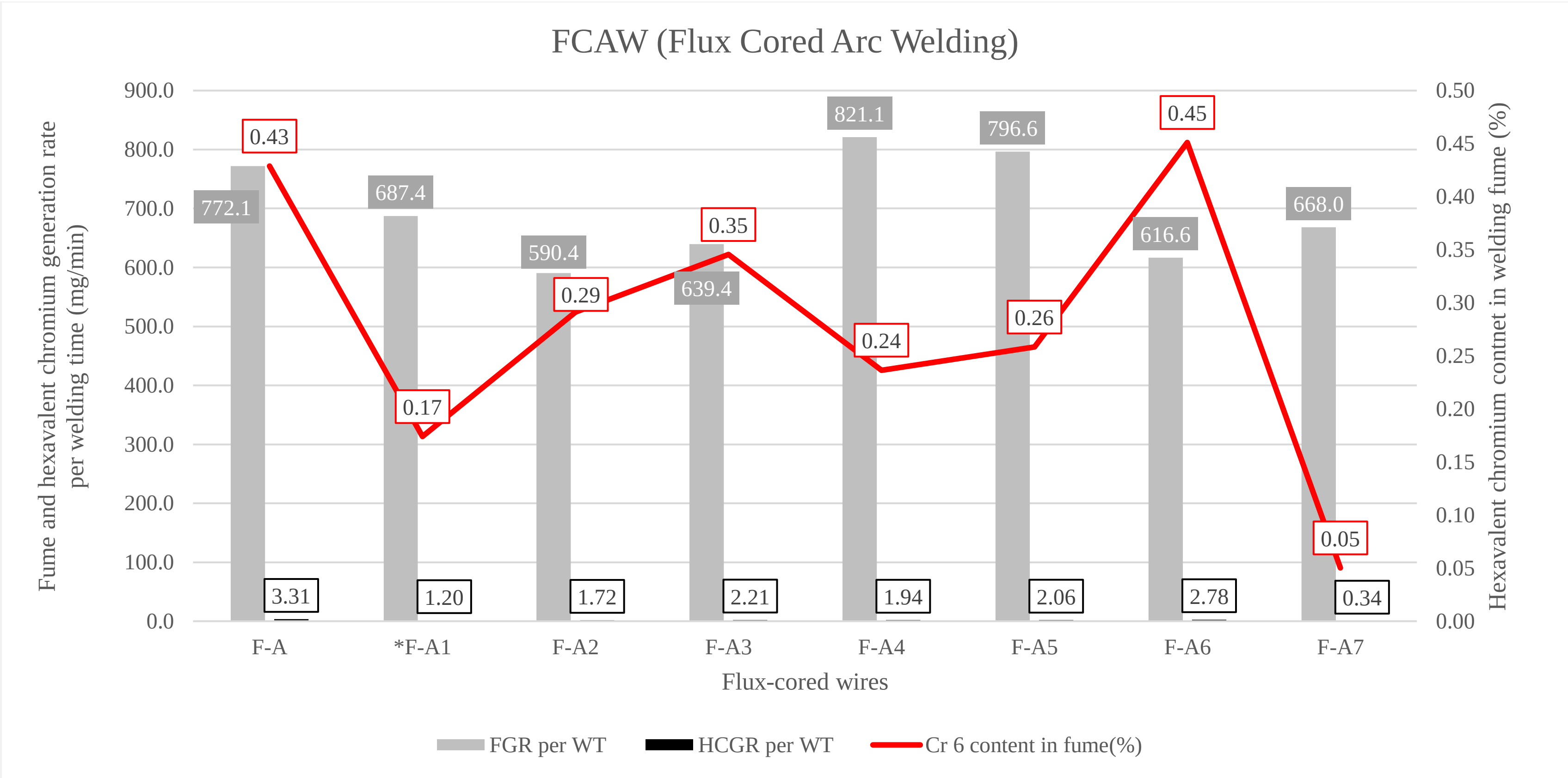


Figure 4. Results of fume generation rate per welding time, hexavalent chromium generation rate per welding time and hexavalent chromium content in welding fume by each of eight flux-cored wires used in this study. (FGR = Fume generation rate, HCGR = Hexavalent chromium generation rate, WT = Welding time)



3.3. Chemical Composition of Welding Filler Material

Analysis of elements and oxide components in the welding filler material of welding rods are shown in Table S6. Further, the graphs showing the analysis results of the content of each element and oxides in the welding filler material of welding are shown in Figure 5 and Figure S2, respectively. Among the elements contained in the welding filler materials of the welding rods, SiO_2 and TiO_2 content was the highest, while Al_2O_3 and CaO content was also higher than other oxides. Most of the test welding filler material in welding rods showed significant differences in the contents of CaO, Fe_2O_3, K_2O, Na_2O, SiO_2, and TiO_2 compared to the base product. Similar results were observed in the oxide components analysis, Si and Ti content was the highest. In particular, as a result of the analysis, it was confirmed that Na, K, and F included in the welding filler materials showed a significant correlation with hexavalent chromium generation according to previous studies. Elements also showed significant differences in the content of Ca, Fe, K, Na, Si, and Ti in most test welding rods compared to the base product. In addition, F showed a difference in the content among welding filler materials of each welding rod, but its instrumental reproducibility was relatively lower than other elements, showing a relatively high standard deviation from the average concentration of each product. Due to this, it is estimated that significance of difference between base welding rod and test products was low.

For FCAW, results of elements and oxide components in flux of flux-cored wires are listed in Table S7. The graphs showing the results of the content of each element and oxides in the flux for flux-cored wire are presented in Figure 5 and Figure S3, respectively. It was confirmed that even in flux, the highest content was SiO_2 and TiO_2 . In contrast to the findings of SMAW, the content of Fe_2O_3 was also high. In the case of elements, the contents of Si, Ti, Fe, and Mn elements were high, and Na, K, and F were also detected above a 1% (Average among wires), which is similar to the findings in oxides. In most of the fluxes for flux cored wires tested in this study, both oxides and elements showed significant differences in the contents of Cr, Fe, Mn, Si, Ti, and Zr compared to the fluxes for base product. F also showed some differences in content between base product and test flux cored wires, but this difference was statistically insignificance.

In this study, chemical component analysis of welding filler material was conducted using (WD)XRF. This was due to the presence of organic compounds above a certain level, as well as the large amount of metal elements and oxides in welding filler. The results of welding filler materials analysis through ICP-MS in the pilot test revealed that the components included in the sample showed interference with argon gas or between other elements, resulting in a high recovery rate and poor repeatability. Similar results were observed while analyzing oxygen and ammonia gas through the DRC mode, and it was estimated that this was due to the influence of organic materials contained in the sample, high-concentration heavy metals, and oxides. Considering these limitations, we conducted the analysis using XRF, which is capable of analyzing F and other organic materials, deriving oxide-type results, and shows no chemical deformation in the pre-treatment process.

Figure 5. Graph presented analysis results of content (%) of each element in welding filler materials in welding rods for SMAW

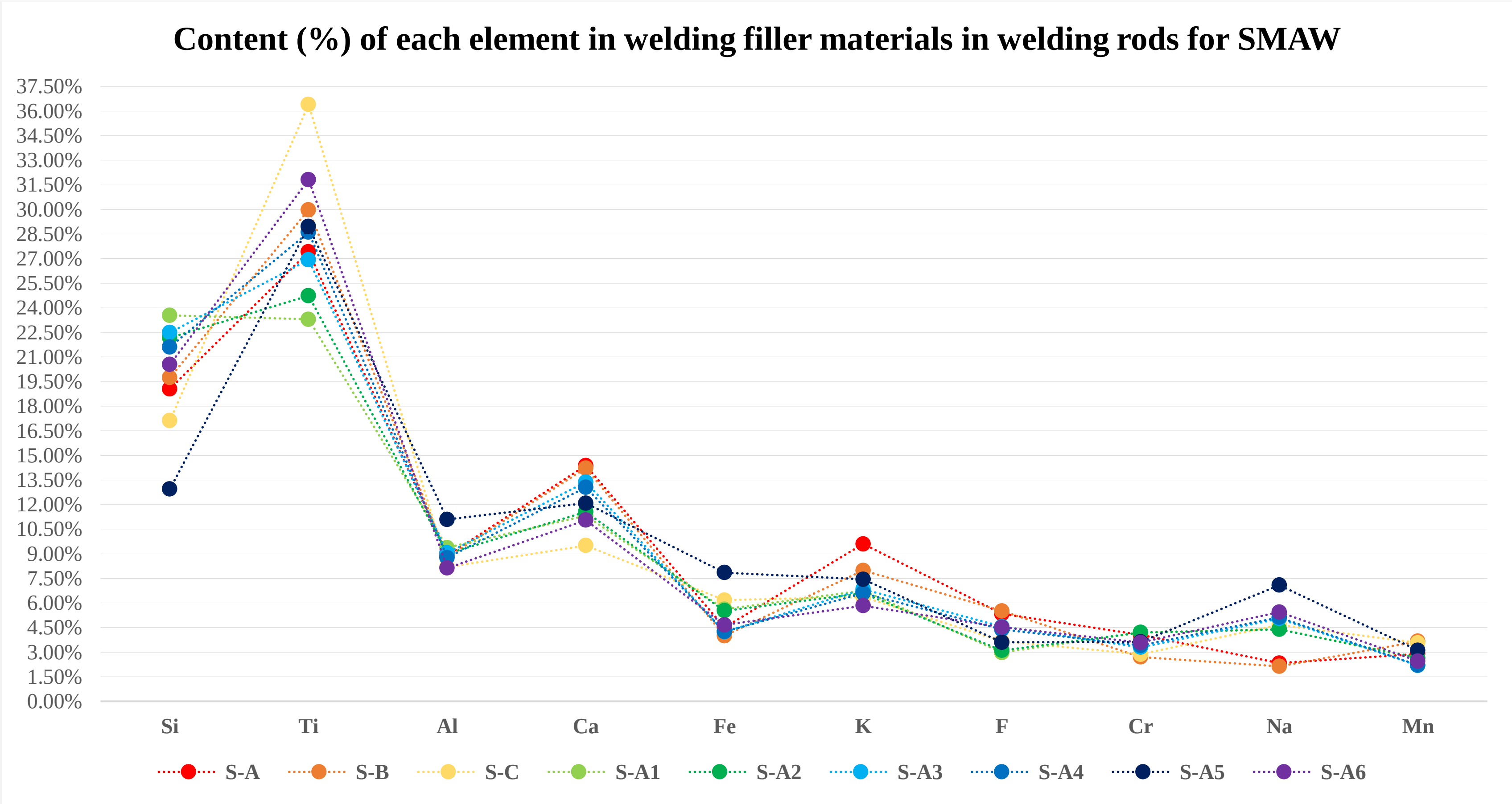
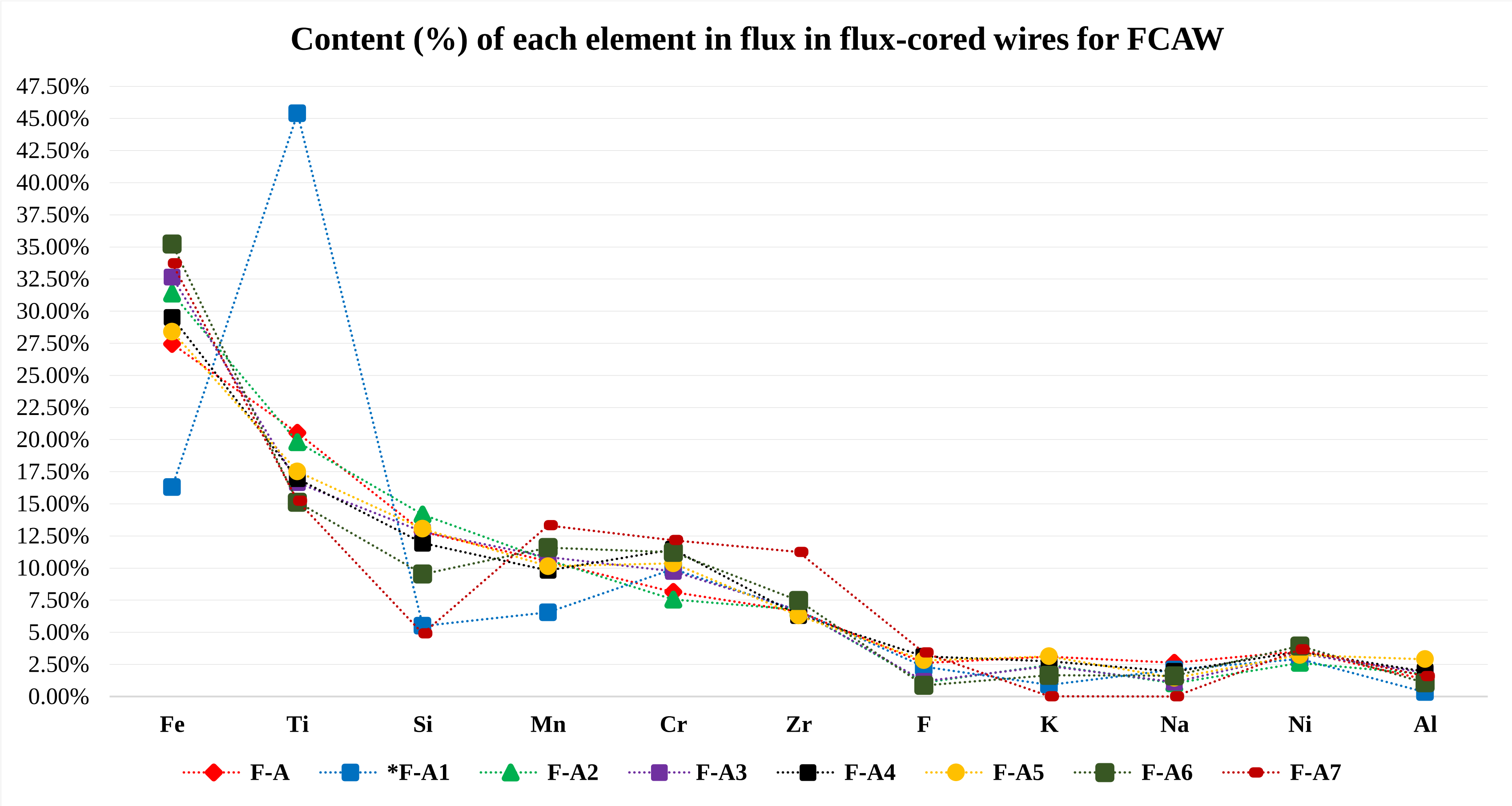


Figure 6. Graph presented analysis results of content (%) of each element in flux in flux-cored wires for FCAW



3.4. Correlation Analysis of Each Component

Table S8 shows the results of Pearson's correlation analysis using elements present in more than 1% of the welding filler materials of welding rods through independent variables. Hexavalent chromium content in welding fume, fume generation rate, and hexavalent chromium generation rate were the dependent variables. Each correlation coefficient value obtained through the analysis was presented as a result, and the criterion for determining the correlation was set to $|r| > 0.6$. For most components except Si, the results obtained using the element analysis and oxide component analysis were similar to those obtained from correlation analysis. In the case of hexavalent chromium content in fumes, F, K, and Ti showed a negative correlation, while Na and SiO_2 showed a positive correlation. For fume generation rate, Na showed a negative correlation, and F, K, Ca, and MnO showed a positive correlation. Finally, for hexavalent chromium generation, Ti showed a negative correlation, and Cr and SiO_2 showed a positive correlation.

Table S9 shows the results of Pearson's correlation analysis of dependent variables because independent variables for elements contained more than 1% of the flux of flux-cored wires. Similar to the SMAW, the criteria for determining the correlation was set to $|r| > 0.6$, and the results of the correlation analysis were similar while using the element analysis and the oxide component analysis. In the case of hexavalent chromium content in welding fume, F and Zr showed a negative correlation, and Na, K, and Si showed a positive correlation. For fume generation rate, F showed a significant positive correlation, and Na and K showed a moderate positive correlation. In the case of hexavalent chromium generation rate, Zr showed a negative correlation, and Na, K, and Si showed a positive correlation.

3.5. Multiple Linear Regression Analysis

A regression model was designed for multiple linear regression analysis based on the results of the component analysis, statistical tests, and correlation analysis of welding filler materials. The hexavalent chromium content in welding fume, fume generation rate per welding time, and hexavalent chromium generation rate per welding time were set as dependent variables, and the components that contained more than 1% in welding filler materials or showed statistical significance in correlation analysis were set as independent variables.

Table S10 shows the results of multiple linear regression analysis using the results of the element content analysis when welding filler materials in welding rods for SMAW were used as an independent variable. For SMAW, the results of the multiple linear regression analysis showed that the p-value of each independent variable and each regression model is low in the three regression models where the fume generation rate per welding time, hexavalent chromium content in welding fume, and hexavalent chromium generation rate per welding time were set as dependent variables, and statistical significance was estimated to be high. However, in all three regression models, the VIF values of the independent variables were high. It was estimated that the suitability of the regression models was low due to the multicollinearity problem caused by mutual interference of the independent variables. In addition, the results obtained by using the findings of oxides component analysis as independent variables are presented in Table S11. When the oxide components analysis data were used as independent variables, it was estimated that TiO_2 and K_2O contributed significantly to the content of hexavalent chromium in welding fume.

In the case of FCAW, the results of multiple linear regression analysis using the analysis results of element content in flux of flux-cored wires as independent variables are shown in Table 5. Although Fe, Si, Ti, Cr, and Mn contributed significantly to the fume generation rate per welding time, it was estimated that the suitability of the regression model was low due to multicollinearity problems caused by interference between variables (VIF>10). However, in the case of the hexavalent chromium content in welding fume and the hexavalent chromium generation rate per welding time, it was confirmed that Na, Ti, and F contributed to the dependent variable significantly. The regression models were estimated to be suitable because of low multicollinearity between variables and a significant p-value of the statistical model. The values of adjusted R^2 for the regression model of hexavalent chromium content in welding fume and hexavalent chromium generation rate per welding time were 0.92 and 0.91, respectively. It was estimated that the contribution of Na, Ti, and F to dependent variables was large in both models. Results derived by using oxide component analysis results as independent variables are shown in Table S12.

In the case of multiple linear regression analysis, there was a difference between the elements analysis results as an independent variable and the oxide component analysis results as an independent variable. Further, most of regression results showed very high covariance among variables. In addition, while including small sample size for multiple linear regression analysis, this statistical method is estimated to be unsuitable for analyzing and interpreting the results of this study.

Table 5. Results of multiple linear regression analysis using elements analysis result of flux in flux-cored wires for FCAW.

	B	SE	β	P-value	VIF
Dependent Variable: Fume generation rate by welding time(mg/min)					
(Intercept)	5376.73	431.91	NA	<0.01	
Fe	-40.80	1.23	-2.77	<0.01	12.87
Si	-54.57	7.49	-2.25	<0.05	176.69
Ti	-52.71	4.16	-6.11	<0.01	431.28
Cr	-55.59	10.03	-1.03	<0.05	63.45
Mn	-119.09	16.04	-2.61	<0.05	229.15
Adjusted R-squared: 0.996					
F-statistic: 370.7 (p-value <0.01)					
Dependent Variable: Hexavalent chromium content in fume(%)					
(Intercept)	0.41	0.05	NA	<0.01	
Na	0.13	0.02	0.77	<0.01	1.19
Ti	-0.01	0.00	-0.53	<0.01	1.19
F	-0.08	0.01	-0.60	<0.01	1.00
Adjusted R-squared: 0.921					
F-statistic: 28.2 (p-value <0.01)					
Dependent Variable: Hexavalent chromium generation rate by welding time(mg/min)					
(Intercept)	2.18	0.35	NA	<0.01	
Na	1.07	0.14	0.94	<0.01	1.19
Ti	-0.05	0.01	-0.60	<0.01	1.19
F	-0.32	0.11	-0.35	<0.05	1.00
Adjusted R-squared: 0.906					
F-statistic: 23.42 (p-value <0.01)					

3.6. Correlation Analysis by Proposed Formula

According to the correlation analysis, none of the specific elements in welding filler materials in both welding rods (in SMAW) and flux-cored wires (in FCAW) showed a strong correlation with fume generation rate, the hexavalent chromium content in welding fume and hexavalent chromium generation rate. Some elements showed significant correlation with each dependent variable. However, the statistical power of significance was not that strong. Moreover, in the case of elements that showed a statistically significant correlation, they were not elements that accounted for a large content in the welding filler materials. In addition, according to the results of multiple linear regression analysis, the statistical significance of each independent variable and each regression model was high in most regression models. However, it was observed that the regression model was limited by the multicollinearity exhibited due to the severe interference effect between independent variables.

Accordingly, it could be inferred from the results that the fume generation rate that the content of hexavalent chromium in welding fumes, and hexavalent chromium generation rate by welding type were not affected by changing the content of some specific elements, but by interaction of many elements. Therefore, we proposed a combined component formula that can reduce fume generation, the content of hexavalent chromium in welding fume, and hexavalent chromium generation under unified welding conditions in SMAW and FCAW.

In the case of SMAW, 11 formulae were proposed in this study, in addition to the 2 formulae, which suggested that there is a correlation between the hexavalent chromium content in welding fume and the hexavalent chromium generation rate through previous studies. Based on the results of welding filler material component analysis, correlation analysis, and multiple linear regression analysis, formulae were designed by combining elements that were both included in the welding filler material above a certain content and showed a statistical correlation with the dependent variables. Thus, after calculating the values derived by the proposed formulae for each welding material, correlation analysis was conducted for each dependent variable with the calculated values as independent variables. The correlation analysis results obtained when data from element component analysis is used as the dependent variable are shown in Table 6, and the results obtained from oxides components analysis data are shown in Table S13. As shown in Table 6, among the proposed eleven formulae, when the dependent variable was fume generation rate, nine formulae showed significant correlation. However, all formulae showed a significant correlation for the content of hexavalent chromium in welding fume, and two formulae showed a significant correlation for hexavalent chromium generation rate.

In the case of FCAW, 10 formulae were proposed in this study, in addition to the two formulae, which suggested that there is a correlation between the hexavalent chromium content in welding fume and the hexavalent chromium generation rate through previous studies. As shown in Table 6, among the proposed 10 formulae, when the dependent variable was fume generation rate, two formulae showed a significant correlation. Moreover, seven formulae showed significant correlation for the content of hexavalent chromium in welding fume, and seven formulae showed a significant correlation for hexavalent chromium generation rate.

Table 6. Pearson's correlation coefficients by each formula with per dependent variable using analysis result of element in welding filler materials in welding rods (for SMAW) and flux-cored wires (for FCAW).

	Pearson's r	**Dependent Variables**						
	For SMAW	Cr 6 in Fume	FGR per DM	FGR per WT	FGR per MU	HCGR per DM	HCGR per WT	HCGR per MU
Independent variables	(Na+K)/F	**0.66**	-0.53	-0.54	**-0.69**	0.36	0.29	0.09
	$((Na+K+Li)*Cr^2)/(Si+4.7*F)$	0.56	-0.05	-0.14	-0.24	**0.68**	**0.61**	0.44
	(F+K+Ca)/(Na)	**-0.67**	**0.85**	**0.82**	**0.91**	-0.08	-0.03	0.07
	(F+K+Ca+Mn)/(Na)	**-0.67**	**0.84**	**0.82**	**0.9**	-0.1	-0.05	0.05
	(Na+Si)/(F+K+Ti)	**0.76**	-0.46	**-0.66**	-0.42	0.5	0.19	0.49
	(Na)/(F+K+Mn+Ti)	**0.75**	**-0.63**	**-0.61**	**-0.75**	0.41	0.4	0.19
	(Na)/(F+K)	**0.65**	**-0.73**	**-0.66**	**-0.82**	0.18	0.21	0
	(Na)/(F+K+Ti)	**0.76**	**-0.63**	**-0.61**	**-0.75**	0.41	0.4	0.19
	(Cr+Mn+Al+Si)/(Ti)	0.59	-0.07	-0.3	-0.08	**0.63**	0.33	**0.6**
	(Na+Si)/(F*K)	**0.76**	**-0.8**	**-0.9**	**-0.75**	0.19	-0.05	0.16
	(Na+Si)/(F*K*Ti)	**0.79**	**-0.63**	**-0.78**	**-0.61**	0.39	0.11	0.34
	(Na+Si)/(F*K*Ti*Mn)	**0.82**	**-0.6**	**-0.78**	-0.58	0.45	0.16	0.41
	((Bi+S+Si)*Cr)/(Ti)	**0.6**	-0.13	-0.38	-0.11	**0.6**	0.26	**0.6**
	Pearson's r	**Dependent Variables**						
	For FCAW	Cr 6 in Fume	FGR per DM	FGR per WT	FGR per MU	HCGR per DM	HCGR per WT	HCGR per MU
Independent variables	(Na+K)/F	**0.86**	-0.37	-0.47	-0.28	**0.64**	**0.69**	**0.65**
	$((Na+K+Li)*Cr^2)/(Si+4.7*F)$	**0.66**	0.04	0.16	0.04	0.58	**0.65**	0.57
	(F+Na+K)	0.28	**0.77**	**0.88**	**0.75**	0.51	0.54	0.5
	(F+K+Ca+Na)	0.28	**0.77**	**0.88**	**0.75**	0.52	0.54	0.51
	(Na+K+Si)/(F+Zr)	**0.72**	0.01	0.09	0.11	**0.65**	**0.73**	**0.65**
	$((Na+K+Si)*Cr^2)/(F+Zr)$	0.55	0.13	0.37	0.21	0.49	0.59	0.49
	(Na+K+Si+Cr)/(F+Zr)	**0.75**	-0.06	0.07	0.03	**0.64**	**0.74**	**0.65**
	(Na+K+Si)/(F+Zr+Cr)	**0.68**	0.07	0.1	0.16	**0.64**	**0.71**	**0.65**
	(Na+K)/(Cr*Ti)	**0.78**	0.42	0.37	0.5	**0.84**	**0.88**	**0.84**
	(Na+K)/(Cr+Ti)	**0.75**	0.45	0.46	0.52	**0.82**	**0.87**	**0.82**
	(Na+K+Si)/(Cr+Ti+Zr)	**0.68**	0.21	0.24	0.33	**0.67**	**0.74**	**0.68**
	(Na+K+Si)/(Cr*Ti*Zr)	**0.66**	0.17	0.18	0.28	**0.64**	**0.7**	**0.65**

* FGR = Fume Generation Rate, HCGR = Hexavalent Chromium Generation Rate / DM = Deposited Metal, WT = Welding Time, MU = Material Usage

4. Discussion

The findings of this study suggested that the fume generation rate, content of hexavalent chromium in welding fume, and the hexavalent chromium generation rate could be reduced without compromising the welding performance by altering the component content of the welding material using SS-308 welding rod in SMAW and SS-308L wire in FCAW. In the case of SMAW, the contents of Ca, Fe, K, Na, Si, and Ti in welding filler material of the welding rod were significantly different from the base welding rod in most test products. In addition, there was a significant difference in Cr, Fe, Mn, Si, Ti, and Zr content in the flux of the flux-cored wires compared to the base product.

In the case of welding fumes designated as a carcinogen to humans, it was evaluated that the fume generation rate per welding time was reduced by up to 26.7% in SMAW (Average reduction rate = 20%) and 23.5% in FCAW (Average reduction rate = 10.8%) than base product. Components that showed statistically significant correlation with the fume generation rate were estimated to be F, K, Ca (positive) and Na (negative) in the case of SMAW. Similarly, with the oxides components analysis results, the components of F, K_2O, MnO, and CaO showed positive correlation with fume generation rate, while Na_2O showed negative correlation with fume generation rate. In the case of FCAW, F showed significant positive correlation with the fume generation rate, whereas Na and K showed moderate positive correlation with the fume generation rate. Similar observations were noted in the oxide analysis results .For both welding types, the higher the content of F and K, the higher the fume generation rate.

It was observed that the hexavalent chromium generation rate per welding time could be reduced to a maximum of 24.8% in SMAW (average reduction rate = 3.4%) and 89.7% in FCAW (average reduction rate = 47.1%). Therefore, the generation of hexavalent chromium could be greatly reduced. In the case of SMAW, components that showed statistical correlation with the hexavalent chromium generation rate were found to be Cr, SiO_2, and Ti. Cr and SiO_2 showed positive correlation, while Ti showed negative correlation. In FCAW, Na, K, and Si showed significant positive correlation, Zr showed significant negative correlation, and F showed moderately negative correlation. This was partially consistent with the findings and suggestions of previous studies which showed that for FCAW welding, the higher the Na and K content, the lower the F content, and the higher the hexavalent chromium content in welding fume and the hexavalent chromium generation rate.

According to the data of this study, in the case of SMAW, the reduction in the amount of hexavalent chromium generation rate was not significant. However, in the case of FCAW, the reduction in hexavalent chromium generation was high. In addition, the welding fume generation rate and the content of hexavalent chromium in welding fume also decreased to a statistically significant level. This suggests that by changing the composition content of the flux injected inside the flux-cored wire, the performance of the welding can be maintained without changing the welding conditions, and the generation of welding fume and hexavalent chromium can be reduced. In the case of SMAW, the welding fume generation rate decreased significantly in most welding rods, but the content of hexavalent chromium in the welding fume increased in most welding rods. However, this means that the amount of hexavalent chromium generated was reduced by a small amount, but the amount of welding fume generated as a first-class carcinogen is significantly reduced. Therefore, if the component content of the welding filler material in the welding rod is adjusted as proposed in this research, it means that the welding performance can be maintained and the generation of harmful substances can be reduced.

This study has three limitations. First, the number of samples was low to perform robust statistical analysis. This study estimated the association between fume and hexavalent chromium generation amount depending on the component content of the welding filler material and flux with nine welding rods with different filler material components and eight wires with different flux components, controlling confounders such as welding condition, base metal, etc. The number of samples for statistical analysis such as correlation analysis and multiple regression analysis was too small, and due to this, it was difficult to derive suitable multiple regression analysis results due to the high covariance among variables. If the data obtained from products made with different filler material and flux components are combined with the data of this study and analyzed statistically in the future, a more accurate association can be estimated. Second, it was difficult to avoid contamination during sample collection. In the case of the SMAW, welding filler material surrounding the outside of the welding rod must be collected, so it must be peeled off with equipment and collected. In this process, there was a possibility of contamination with other heavy metals, leading to inaccuracies in analysis. Third, there were some substances with poor reproducibility due to the characteristics of the analysis instrument. In the case of F, which was analyzed among the components of welding filler materials in this study, the standard deviation was large due to poor reproducibility between the samples when analyzing XRF devices, so the statistical difference between the test product and the base product was not significant. In addition, errors in the accuracy of the analysis would have had a negative effect on the statistical estimation of association.

In this study, we discussed new aspects that could not be presented in previous studies. First, it is recommended to use a PTFE-D filter rather than a GFF filter that is used to evaluate the fume generation rate when collecting fume for evaluating the hexavalent chromium content in welding fume. This is to prevent silicon oxides such as SiO_2 that are present on the surface of the GFF filter from being collected as impurities when collecting fume. In this study, when analyzing the hexavalent chromium content in welding fume using the PTFE-D filter, the standard deviation between samples from same welding materials was very low ensuring high reproducibility. Table S14 presents the data of the reproducibility test through the standard deviation between the analyzed samples when hexavalent chromium collected by the two different filters was analyzed through the same pretreatment method and instrument as in the pilot study. Second, it is recommended to use an instrument such as XRF instead of an instrument such as ICP-MS that may cause chemical denaturation during pre-treatment and interference by other substances during analysis. In this study, when ICP-MS was used to analyze welding filler material components, even though the DRC mode was used, a suitable analysis result could not be obtained with such high recovery and low repeatability due to the interference of other elements. However, it showed high reproducibility and repeatability when analyzed using XRF. Additionally, XRF was used, not only elements but also oxide component analysis results could be derived. Third, statistical estimation by correlation analysis and multiple linear regression analysis showed that only a specific element content did not strongly contribute to the fume and hexavalent chromium generation and hexavalent chromium content in welding fume. The complex content change of several components contributes to reduction of the variables. That is, in order to reduce the amount of fume generated or the amount of hexavalent chromium generated, a comprehensive change is required, not the change in the content of a specific element. It was due to multicollinearity, mutual interference between elements in welding filler materials induced by strong correlation among content of them. Fourth, in the case of SMAW, in order to reduce hexavalent chromium generation rate, a reduction in fume generation rate is suggested. Furthermore, for FCAW, it is recommended to reduce the content of hexavalent chromium in the welding fume. This is due to the characteristics of each welding type. About SMAW, the fume generation rate per welding time is relatively small due to the characteristics of welding, but the hexavalent chromium content in welding fumes is high. Therefore, it is difficult to reduce the hexavalent chromium content among fumes, but it is relatively easy to reduce the amount of fumes generated per welding time. In addition, FCAW has a relatively high fume generation rate per welding time, and the hexavalent chromium content in welding fume is low. Therefore, it is difficult to reduce the fume generation rate per welding time, but it is relatively easy to reduce the hexavalent chromium content during fume.

Finally, it is estimated that the chromium oxidized by receiving the arc formed during the welding contributes to the content of hexavalent chromium in welding fume and the hexavalent chromium generation rate during welding. Furthermore, we estimated that the higher the content of components such as Na and K with lower electronegativity than that of chromium, the more the chromium is easily oxidized to hexavalent chromium, and the higher the content of F having a higher electronegativity than chromium, the lesser the hexavalent chromium is generated. A previous study postulated the mechanism of hexavalent chromium formation in SMAW, wherein chromium is oxidized to form hexavalent chromates by reacting with alkali oxides in the welding filler material when the welding material is melted and oxidized together with various components in the slag (Kopen., et al., 1981). However, elements among the welding materials are not present in an element form but in form of a composite compound. Therefore, it is recommended to manufacture the welding material with components that can suppress oxidation of chromium and have a higher electronegativity than metal chromium and chromium compounds, by considering oxidation ability and electronegativity of the compound.

5. Conclusions

The results of this study confirmed that the generation rate of welding fume and hexavalent chromium can be reduced without compromising the welding performance by changing the components in the welding material of welding rods and flux-cored wires. This means that the amount of welding fume and hexavalent chromium, which have been widely known to cause cancer in humans with IARC designated Group 1 carcinogens, can be reduced.

For instance, if a welding filler material of welding materials is manufactured by referring to 11 component-combination formulas for shielded metal arc welding and 10 component-combination formulas for flux-cored arc welding, it could be possible to reduce the fume and hexavalent chromium generation rate. In particular, reduction of hexavalent chromium generation rate is possible by effectively reducing the fume generation rate for SMAW and the content of hexavalent chromium in welding fume for FCAW. Additionally, the hexavalent chromium generation rate during welding may also be reduced if the welding material includes more components capable of suppressing oxidation of chromium to hexavalent chromium and having higher electronegativity than metal chromium or chromium compound.

Although this study does not cover all welding types, as SMAW is limited to SS-308 and FCAW is limited to SS-308L, and the number of welding materials used in the study is small, it is possible to provide a scientific basis to reduce the generation of carcinogens in workplace. In addition, this study proposed to alter the welding filler material component rather than modifying the welding conditions to reduce the rate of fume generation and hexavalent chromium generation. In many cases, it is inevitable to change welding conditions due to work characteristics, so it was intended to fundamentally improve workers' exposure to harmful substances by proposing materials that generate relatively low toxic substances.

A fundamental improvement plan can be proposed for reducing the amount of harmful substances exposed to welding workers by using a product that generates less fume and hexavalent chromium is used in a workplace using the data from this study.

6. References

K. Weman. (2012). Welding Processes Handbook Second edition. Woodhead Publishing. UK.

Ashley Newton., et al. (2021). Journal of Aerosol Science.

Antonini, J. (2008). Health effects of welding. Critical Reviews in Toxicology, 33(1), 61–103. Retrieved from http://www.tandfonline.com/doi/full/10.1080/713611032.

Ennan, A. A., Kiro, S. A., Oprya, M. V., & Vishnyakov, V. I. (2013). Particle size distribution of welding fume and its dependency on conditions of shielded metal arc welding. *Journal of Aerosol Science, 64*, 103–110. https://doi.org/10.1016/j.jaerosci.2013.06.006

Vishnyakov, V. I., Kiro, S. A., & Ennan, A. A. (2013). Formation of primary particles in welding fume. *Journal of Aerosol Science, 58*, 9–16. https://doi.org/10.1016/j. jaerosci.2012.12.003

Hewitt, P. J. and A. A. Hirst : A system approach to the control of welding fumes at source. *Ann. Occup. Hyg.* 37(3):297-306 (1993).

Palmer, W. G. and J. C. Eaton : *Effect of welding on health IX*. Miami, Fl; American Welding Society, 1994. pp. 19-29.

Palmer, W. G. : *Effect of welding on health IV*. Miami, Fl; American Welding Society, 1983. Pp. 1-10.

윤충식. (1999). 용접공정의 흄 발생량과 공기중 6가 크롬에 관한 연구. 박사학위논문, 서울대학교, 서울.

Koppen, M., T. Gustafsson, P. Kalliomaki and L. Pyy : Chromium and nickel aerosols in stainless steel manufacturing, grinding and welding. *Am. Ind. Hyg. Assoc. J.* 42:596-601 (1981).

Floros, N., 2018. Welding fume main compounds and structure. Weld. World 62, 311–316.

McCarrick, S., Wei, Z., Moelijker, N., Derr, R., Persson, K.-A., Hendriks, G., Odnevall Wallinder, I., Hedberg, Y.S., Karlsson, H.L., 2019. High variability in toxicity of welding fume nanoparticles from stainless steel in lung cells and reporter cell lines: the role of particle reactivity and solubility. Nanotoxicology 13, 1293–1309.

Mei, N., Belleville, L., Cha, Y., Olofsson, U., Odnevall Wallinder, I., Persson, K.-A., Hedberg, Y., 2018. Size-separated particle fractions of stainless steel welding fume particles – a multi-analytical characterization focusing on surface oxide speciation and release of hexavalent chromium. J. Hazard. Mater. 342, 527–535.

Tandon, R., Payling, R., Chenhall, B., Crisp, P., Ellis, J., Baker, R., 1985. Application of X-ray photoelectron spectroscopy to the analysis of stainless-steel welding aerosols. Appl. Surf. Sci. 20, 527–537.

Floros, N., 2016. Hexavalent chromium in stainless steel solid wire welding fumes, in: Commission VIII - Health, Safety, and Environment, International Institute of Welding.

Yoon, C.S. (2003). Fume Generation and Content of Total Chromium and Hexavalent Chromium in Flux-cored Arc Welding. The Annals of Occupational Hygiene 47, 671–680.. doi:10.1093/annhyg/meg0632

Ashley, K. (2009). Evaluation of sequential extraction procedures for soluble and insoluble hexavalent chromium compounds in workplace air samples. J Environ Monit, 11(2), 318-325. https://doi.org/10.1039/b812236a

Yoon, C.S. (2003). 플럭스코어드아크 용접 중 발생하는 총 크롬 및 6가 크롬의 함량 변화. Journal of Korean Society of Occupational and environmental hygiene v.10 no.1 , 2000년, pp.32 – 44

Yoon, C.S., 2003. 초음파 전처리에 의한 용접 흄중 6가 크롬의 분석. Analytical science & technology v.12 no.5 , 1999년, pp.447 – 459

CDC. (2018). NIOSH Manual of Analytical Methods (NMAM) 5th Edition, US.

ISO 15011-4:2017 & 16740:2005 & 9516

KS D 0064 & 1654 & 3503 & 3515, KS M 0050 & 0017

Scarselli, A., Binazzi, A., Marzio, D. D., Marinaccio, A., & Iavicoli, S. (2012). Hexavalent chromium compounds in the workplace: assessing the extent and magnitude of occupational exposure in Italy. J Occup Environ Hyg, 9(6), 398-407.

Costa, M., & Klein, C. B. (2006). Toxicity and carcinogenicity of chromium compounds in humans. Crit Rev Toxicol, 36(2), 155-163. https://doi.org/10.1080/10408440500534032

Kim, C., Moon, D., & Moon, S. (2012). Statistical Analysis of World Welding Consumables Market. Journal of the Korean Welding and Joining Society, 30(5), 4-8. https://doi.org/10.5781/kwjs.2012.30.5.398

ACGIH TLV (2019).

Voitkecivh, V. : Chapter 2. Welding fume properties. In welding fumes-formation, properties and biological effects. England; Abington Publishing, 1995. pp. 18-77

Kim, J., Seo, S., Kim, Y., & Kim, D. H. (2018). Review of carcinogenicity of hexavalent chrome and proposal of revising approval standards for an occupational cancers in Korea. *Ann Occup Environ Med, 30, 7. https://doi.org/10.1186/s40557-018-0215-2*

Dennis, J. H., French, M. J., Hewitt, P. J., Mortazavi, S. B., & Redding, C. A. (2002). Control of occupational exposure to hexavalent chromium and ozone in tubular wire arc-welding processes by replacement of potassium by lithium or by addition of zinc. *Ann Occup Hyg*, *46*(1), 33-42.

https://doi.org/10.1093/annhyg/mef024

Gu, X., Cui, Z., Gu, X., & Shao, J. (2021). Wire-Feeding Laser Welding of Copper/Stainless Steel Using Different Filler Metals. *Materials (Basel)*, *14*(9). https://doi.org/10.3390/ma14092122

Markovic, S., Arsic, D., Nikolic, R. R., Lazic, V., Ratkovic, N., Hadzima, B., Szmidla, J., & Ulewicz, R. (2021). Analysis of the Welding Type and Filler Metal Influence on Performance of a Regenerated Gear. *Materials (Basel)*, *14*(6). https://doi.org/10.3390/ma14061496

McCarrick, S., Wei, Z., Moelijker, N., Derr, R., Persson, K. A., Hendriks, G., Odnevall Wallinder, I., Hedberg, Y., & Karlsson, H. L. (2019). High variability in toxicity of welding fume nanoparticles from stainless steel in lung cells and reporter cell lines: the role of particle reactivity and solubility. *Nanotoxicology*, *13*(10), 1293-1309. https://doi.org/10.1080/17435390.2019.1650972

Supplementary Materials

Figure S 1. Process diagram of welding in fume hood for evaluating fume generation rate and hexavalent chromium generation rate in this study.

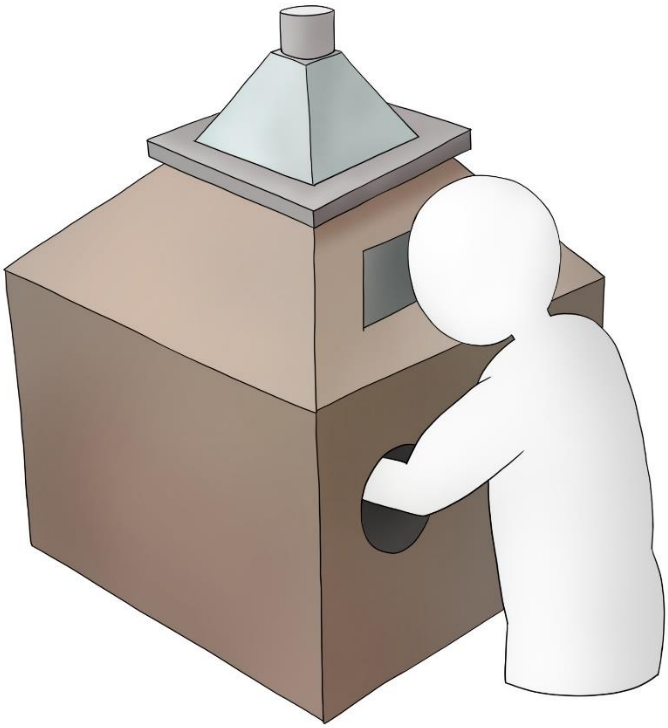


Table S 1. Analytical condition and parameter for hexavalent chromium analysis by IC-UV.

Parameter	Analytical Condition
Instrument	ICS-1100, Thermo fisher Scientific
Column	Dionex IonPac AS7 IC Column
Flow rate	1.0 mL/min
UV Detector	540nm wavelength

Table S 2. Analytical condition and parameter for oxides components and elements analysis by XRF.

Parameter	Analytical Condition
Instrument	XRF S8-Tiger(Series 1), Bruker-AXS
Sample definition	Quant Express
Material	Oxides(trace), Elements(trace)
Preparation	Solid
Mode	Vacuum
Diameter	34mm
Method	Best Detection-Vac34mm
Pressure Forming	
Press force	25t
Holding time	1 min

Table S 3. Fume generation test result of each welding material in controlled welding condition for different welding types. (AM±SD)

Type	Product	Welding Time (S)	Sampling Time(S)	Collected Fume (mg)	Deposited Metal (g)	Material usage (g)	Speed (Kg/h)	Melting Efficiency (%)	Fume Generation Rate per		
									Deposited Metal (mg/g)	Welding Time (mg/min)	Material Usage (mg/g)
SMAW (n=9)	S-A	60	200	72.3 ± 4.5	4.7 ± 0.1	7.3 ± 0.4	1.13 ± 0.02	64.5 ± 2.2	15.4 ± 1.3	289.3 ± 18.0	10.0 ± 1.2
	S-B			71.3 ± 9.0	5.0 ± 0.1	7.4 ± 0.1	1.21 ± 0.01	67.7 ± 0.9	14.2 ± 1.7	285.3 ± 35.9	9.6 ± 1.3
	S-C			53.0 ± 3.0	4.9 ± 0.2	7.8 ± 0.2	1.18 ± 0.04	63.5 ± 0.9	10.7 ± 0.5	212.0 ± 12.0	6.8 ± 0.4
	S-A1			49.5 ± 6.4	4.6 ± 0.2	7.1 ± 0.3	1.10 ± 0.04	64.3 ± 0.4	11.0 ± 1.1	198.0 ± 25.5	7.1 ± 0.6
	S-A2			55.7 ± 4.9	4.6 ± 0.1	7.2 ± 0.2	1.10 ± 0.01	63.7 ± 0.7	12.2 ± 0.9	222.7 ± 19.7	7.8 ± 0.6
	S-A3			55.5 ± 2.1	4.8 ± 0.2	7.7 ± 0.3	1.16 ± 0.05	62.5 ± 1.5	11.6 ± 1.1	222.0 ± 8.5	7.3 ± 1.1
	S-A4			56.7 ± 5.1	4.6 ± 0.1	7.2 ± 0.0	1.10 ± 0.01	63.4 ± 0.8	12.4 ± 1.2	226.7 ± 20.5	7.9 ± 0.7
	S-A5			63.7 ± 5.7	5.0 ± 0.1	8.4 ± 0.3	1.21 ± 0.03	59.7 ± 1.0	12.7 ± 1.1	254.7 ± 22.7	7.6 ± 0.6
	S-A6			57.3 ± 5.9	4.9 ± 0.1	7.0 ± 0.2	1.17 ± 0.01	69.2 ± 2.0	11.8 ± 1.2	229.3 ± 23.4	8.1 ± 0.6
FCAW (n=8)	F-A	30	200	183.2 ± 4.6	14.9 ± 0.4	17.0 ± 0.3	3.76 ± 0.10	87.2 ± 1.1	12.3 ± 0.4	772.1 ± 20.0	10.8 ± 0.4
	*F-A1			165.6 ± 11.3	18.7 ± 1.5	23.2 ± 1.9	4.65 ± 0.22	80.3 ± 0.2	8.9 ± 0.1	687.4 ± 22.9	7.1 ± 0.1
	F-A2			138.7 ± 3.5	17.4 ± 0.1	19.8 ± 0.4	4.45 ± 0.04	87.7 ± 1.5	8.0 ± 0.2	590.4 ± 6.5	7.0 ± 0.2
	F-A3			155.3 ± 1.8	18.2 ± 0.1	20.6 ± 0.5	4.50 ± 0.04	88.3 ± 2.2	8.5 ± 0.1	639.4 ± 4.0	7.5 ± 0.2
	F-A4			192.9 ± 20.7	17.6 ± 0.1	20.5 ± 1.0	4.50 ± 0.08	85.9 ± 1.5	10.9 ± 1.2	821.1 ± 91.9	9.4 ± 1.0
	F-A5			187.8 ± 12.1	17.7 ± 1.1	20.1 ± 0.7	4.51 ± 0.31	88.1 ± 1.5	10.6 ± 0.2	796.6 ± 52.6	9.3 ± 0.6
	F-A6			147.5 ± 6.6	15.9 ± 0.4	18.1 ± 0.6	3.98 ± 0.05	88.7 ± 1.9	9.3 ± 0.3	616.6 ± 17.5	8.2 ± 0.4
	F-A7			158.5 ± 1.9	15.9 ± 1.2	18.3 ± 1.5	4.01 ± 0.20	86.6 ± 1.4	10.0 ± 0.6	668.0 ± 7.1	8.7 ± 0.3

* S-B, S-C : Welding rods product manufactured by other manufacturer, F-A1 : Flux-cored wire for all posture(AP) welding

Table S 4. Mechanical Property of weld metal by AWS A5.4 E308-16 standard for STS-308 welding rod.

Product	Tensile Strength (MPa)	Elongation (%)
Requirements	**≥ 550**	**≥ 30**
S-A	609.0	50.8
S-B	598.0	53.0
S-C	620.0	45.0
S-A1	614.0	45.7
S-A2	613.0	47.6
S-A3	635.0	47.6
S-A4	621.0	48.4
S-A5	604.0	50.4
S-A6	-	-

Table S 5. Mechanical Property of weld metal by AWS A5.22 E308LT0-1/4 standard for STS-308L welding wire.

Product	Tensile Strength (MPa)	Elongation (%)
Requirements	**≥ 550**	**≥ 30**
F-A	579.0	41.4
***F-A1**	570.0	44.0
F-A2	570.2	41.7
F-A3	594.2	36.9

Table S 6. Chemical components contents of oxides and elements in welding filler material in welding rods for SMAW.

Oxides	Al_2O_3		BaO		CaO		Cr_2O_3		F		Fe_2O_3		K_2O		MnO		Na_2O		SiO_2		TiO_2	
	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value
S-A	12.24%	Standard	N.D	Standard	11.60%	Standard	2.94%	Standard	4.37%	Standard	3.14%	Standard	7.10%	Standard	1.84%	Standard	2.40%	Standard	28.42%	Standard	24.56%	Standard
S-B	12.06%	0.50	N.D	-	11.45%	0.37	1.94%	<0.05	4.25%	0.94	2.76%	0.09	5.87%	<0.01	2.31%	0.11	2.19%	0.80	29.29%	<0.01	26.69%	<0.01
S-C	11.09%	<0.05	N.D	-	7.92%	<0.01	2.08%	<0.05	2.87%	0.44	4.31%	<0.01	4.31%	<0.01	0.55%	<0.01	4.69%	<0.05	25.23%	<0.01	33.33%	<0.01
S-A1	12.47%	0.41	2.52%	-	8.96%	<0.01	2.97%	0.91	2.58%	0.38	3.79%	<0.05	4.79%	<0.01	1.62%	0.42	4.48%	<0.05	33.74%	<0.01	20.43%	<0.01
S-A2	12.06%	0.51	2.54%	-	9.26%	<0.01	3.02%	0.76	2.62%	0.39	3.78%	<0.05	4.75%	<0.01	1.68%	0.55	4.48%	<0.05	32.08%	<0.01	21.97%	<0.01
S-A3	12.19%	0.85	N.D	-	10.44%	<0.01	2.26%	0.06	3.61%	0.66	2.79%	0.10	4.82%	<0.01	1.32%	0.12	5.19%	<0.05	32.48%	<0.01	23.02%	<0.01
S-A4	11.74%	0.12	21 PPM	-	10.31%	<0.01	2.37%	0.09	3.65%	0.67	2.83%	0.13	4.70%	<0.01	1.34%	0.13	5.20%	<0.05	31.23%	<0.01	24.76%	0.14
S-A5	12.24%	-	0.03%	-	8.81%	<0.01	2.14%	<0.05	2.62%	0.38	4.40%	<0.01	5.01%	<0.01	1.61%	0.39	5.89%	<0.01	33.21%	<0.01	22.32%	<0.01
S-A6	10.92%	<0.01	N.D	-	8.88%	<0.01	2.52%	0.17	3.63%	0.66	3.14%	-	4.21%	<0.01	1.51%	0.26	5.51%	<0.05	29.83%	<0.01	28.04%	<0.01

Elements	Al		Ba		Ca		Cr		F		Fe		K		Mn		Na		Si		Ti	
	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value
S-A	8.88%	Standard	N.D	Standard	14.38%	Standard	4.05%	Standard	5.34%	Standard	4.51%	Standard	9.60%	Standard	2.89%	Standard	2.33%	Standard	19.06%	Standard	27.42%	Standard
S-B	8.78%	0.70	N.D	-	14.22%	0.34	2.70%	<0.01	5.51%	0.94	4.00%	<0.05	7.98%	<0.01	3.66%	<0.05	2.13%	0.81	19.74%	<0.05	29.98%	<0.01
S-C	8.20%	0.06	N.D	-	9.50%	<0.01	2.87%	<0.05	3.67%	0.55	6.17%	<0.01	6.36%	<0.01	3.56%	<0.05	4.66%	<0.05	17.12%	<0.01	36.40%	<0.01
S-A1	9.37%	0.12	4.19%	-	11.32%	<0.01	4.19%	0.60	2.97%	0.44	5.61%	<0.01	6.75%	<0.01	2.60%	0.30	4.40%	<0.05	23.54%	<0.01	23.30%	<0.01
S-A2	9.01%	0.63	4.16%	-	11.55%	<0.01	4.20%	0.57	3.10%	0.38	5.52%	<0.01	6.60%	<0.01	2.66%	0.40	4.39%	<0.05	22.18%	<0.01	24.74%	<0.01
S-A3	9.05%	0.53	N.D	-	13.37%	<0.01	3.29%	<0.05	4.55%	0.76	4.23%	0.16	6.84%	<0.01	2.18%	0.05	5.05%	<0.05	22.49%	<0.01	26.93%	<0.05
S-A4	8.76%	0.66	N.D	-	13.05%	<0.01	3.41%	0.07	4.38%	0.71	4.25%	0.19	6.60%	<0.01	2.20%	0.06	5.12%	<0.05	21.61%	<0.01	28.61%	<0.01
S-A5	11.09%	<0.01	N.D	-	12.08%	<0.01	3.62%	0.18	3.60%	0.55	7.85%	<0.01	7.44%	<0.01	3.11%	0.41	7.08%	<0.01	12.94%	<0.01	28.96%	<0.01
S-A6	8.13%	<0.05	N.D	-	11.05%	<0.01	3.58%	0.14	4.52%	0.75	4.66%	0.40	5.83%	<0.01	2.45%	0.15	5.44%	<0.05	20.54%	<0.01	31.82%	<0.01

* Conc. : Concentration / AM : Arithmetic mean / P-value : results of independent two-sample T-test.

Figure S 2. Graph presented analysis results of content (%) of each oxide in welding filler materials in welding rods for SMAW.

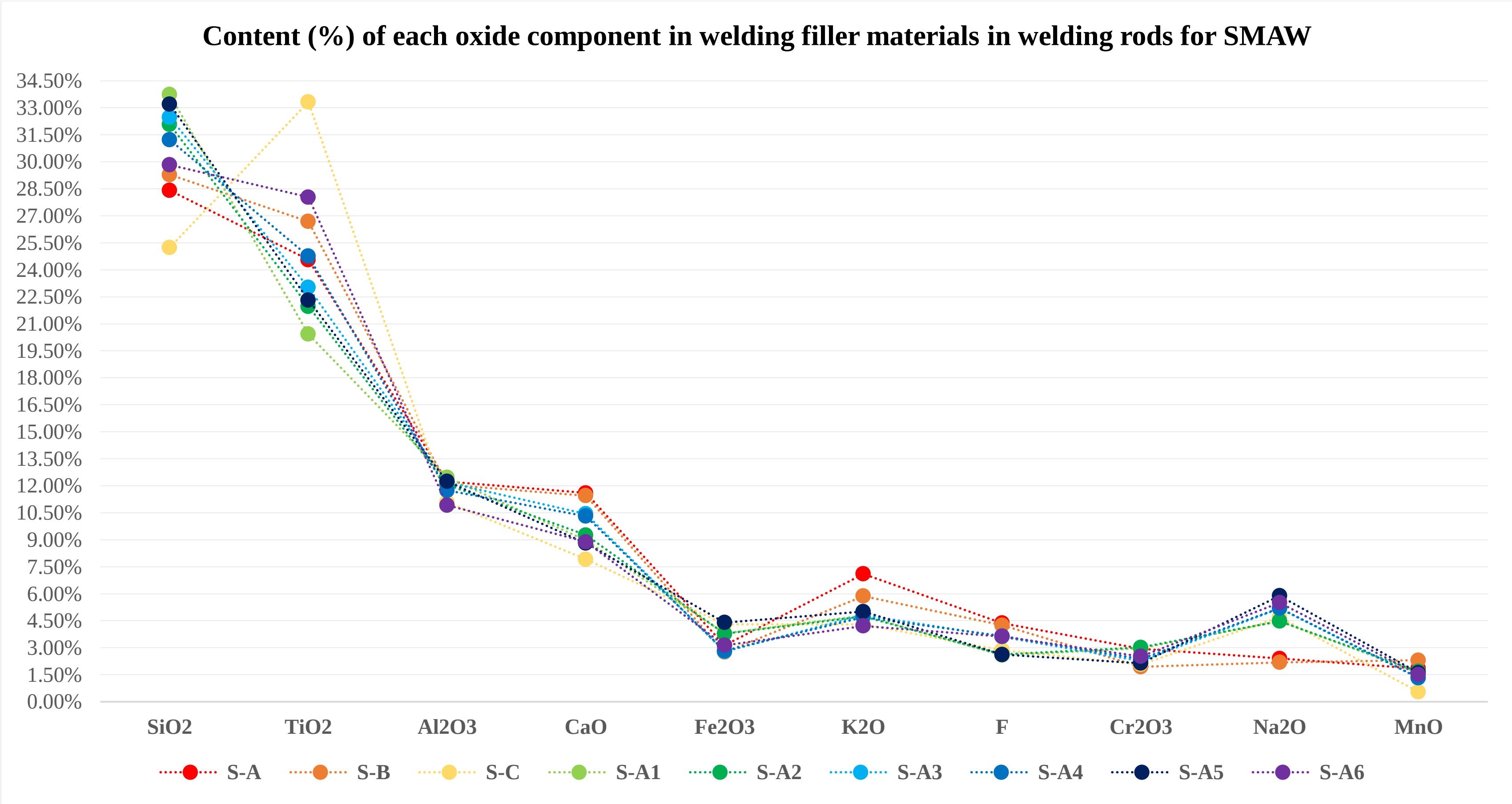


Table S 7. Chemical components contents of oxides and elements in flux in flux-cored wires for FCAW.

Oxides	Al2O3		Cr2O3		F		Fe2O3		K2O		MnO		Na2O		NiO		SiO2		TiO2		ZrO2	
	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value
F-A	1.89%	Standard	7.41%	Standard	2.48%	Standard	23.64%	Standard	2.53%	Standard	8.33%	Standard	2.75%	Standard	2.57%	Standard	20.34%	Standard	22.34%	Standard	5.00%	Standard
*F-A1	0.50%	0.31	8.85%	<0.01	2.29%	0.93	13.94%	<0.01	0.75%	<0.05	5.13%	<0.01	2.25%	0.58	2.16%	0.07	8.94%	<0.01	48.95%	<0.01	5.11%	0.13
F-A2	2.47%	0.42	6.80%	<0.05	1.22%	0.63	26.75%	<0.01	1.97%	0.14	8.33%	-	1.09%	0.21	1.91%	<0.05	22.39%	<0.01	21.25%	<0.01	5.05%	0.43
F-A3	2.64%	0.31	8.99%	<0.01	1.33%	0.64	28.35%	<0.01	1.93%	0.13	8.68%	<0.05	1.17%	0.21	2.47%	0.56	20.32%	0.93	18.27%	<0.01	5.11%	0.13
F-A4	2.76%	0.24	10.60%	<0.01	2.95%	0.81	25.68%	<0.01	2.25%	0.40	7.88%	<0.05	2.05%	0.45	2.59%	0.90	19.02%	<0.01	18.68%	<0.01	4.83%	<0.05
F-A5	4.10%	<0.05	9.42%	<0.01	2.88%	0.84	24.26%	<0.01	2.53%	-	7.99%	<0.05	1.50%	0.25	2.35%	0.24	20.56%	0.34	18.99%	<0.01	4.70%	<0.01
F-A6	1.53%	0.65	10.77%	<0.01	0.85%	0.58	31.83%	<0.01	1.39%	<0.05	9.64%	<0.01	1.71%	0.32	3.04%	<0.05	15.42%	<0.01	17.15%	<0.01	5.97%	<0.01
F-A7	2.39%	0.50	12.03%	<0.01	3.30%	0.68	31.73%	<0.01	61 PPM	<0.01	11.48%	<0.01	N.D	<0.05	2.98%	0.06	8.18%	<0.01	17.66%	<0.01	9.46%	<0.01

Elements	Al		Cr		F		Fe		K		Mn		Na		Ni		Si		Ti		Zr	
	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value	Conc. (AM)	p-value
F-A	1.33%	Standard	8.13%	Standard	2.61%	Standard	27.45%	Standard	3.10%	Standard	10.53%	Standard	2.63%	Standard	3.51%	Standard	12.82%	Standard	20.52%	Standard	6.63%	Standard
*F-A1	0.34%	0.44	9.92%	<0.01	2.32%	0.93	16.30%	<0.01	0.91%	<0.05	6.55%	<0.01	2.09%	0.55	2.91%	<0.05	5.50%	<0.01	45.40%	<0.01	6.67%	0.52
F-A2	1.74%	0.56	7.55%	<0.05	1.07%	0.66	31.37%	<0.01	2.45%	0.10	10.64%	0.36	1.03%	0.22	2.62%	<0.01	14.16%	<0.01	19.80%	<0.01	6.76%	0.09
F-A3	1.86%	0.45	9.74%	<0.01	1.19%	0.67	32.65%	<0.01	2.36%	0.08	10.85%	<0.05	1.12%	0.23	3.35%	0.37	12.83%	0.96	16.64%	<0.01	6.70%	0.29
F-A4	1.94%	0.39	11.46%	<0.01	3.12%	0.85	29.51%	<0.01	2.74%	0.29	9.82%	<0.01	1.95%	0.46	3.49%	0.90	11.94%	<0.05	16.96%	<0.01	6.31%	<0.01
F-A5	2.90%	0.06	10.36%	<0.01	2.82%	0.94	28.40%	<0.01	3.12%	0.95	10.14%	<0.05	1.44%	0.27	3.23%	0.15	13.05%	0.32	17.51%	<0.01	6.29%	<0.01
F-A6	1.06%	0.74	11.23%	<0.01	0.86%	0.63	35.22%	<0.01	1.65%	<0.05	11.59%	<0.01	1.61%	0.33	3.93%	0.05	9.53%	<0.01	15.13%	<0.01	7.47%	<0.01
F-A7	1.59%	0.72	12.17%	<0.01	3.41%	0.77	33.72%	<0.01	71 PPM	<0.01	13.32%	<0.01	N.D	<0.05	3.66%	0.40	4.90%	<0.01	15.23%	<0.01	11.25%	<0.01

* Conc. : Concentration / AM : Arithmetic mean / P-value : results of independent two-sample T-test.

Figure S 3. Graph presented analysis results of content (%) of each oxide in flux in flux-cored wires for FCAW.

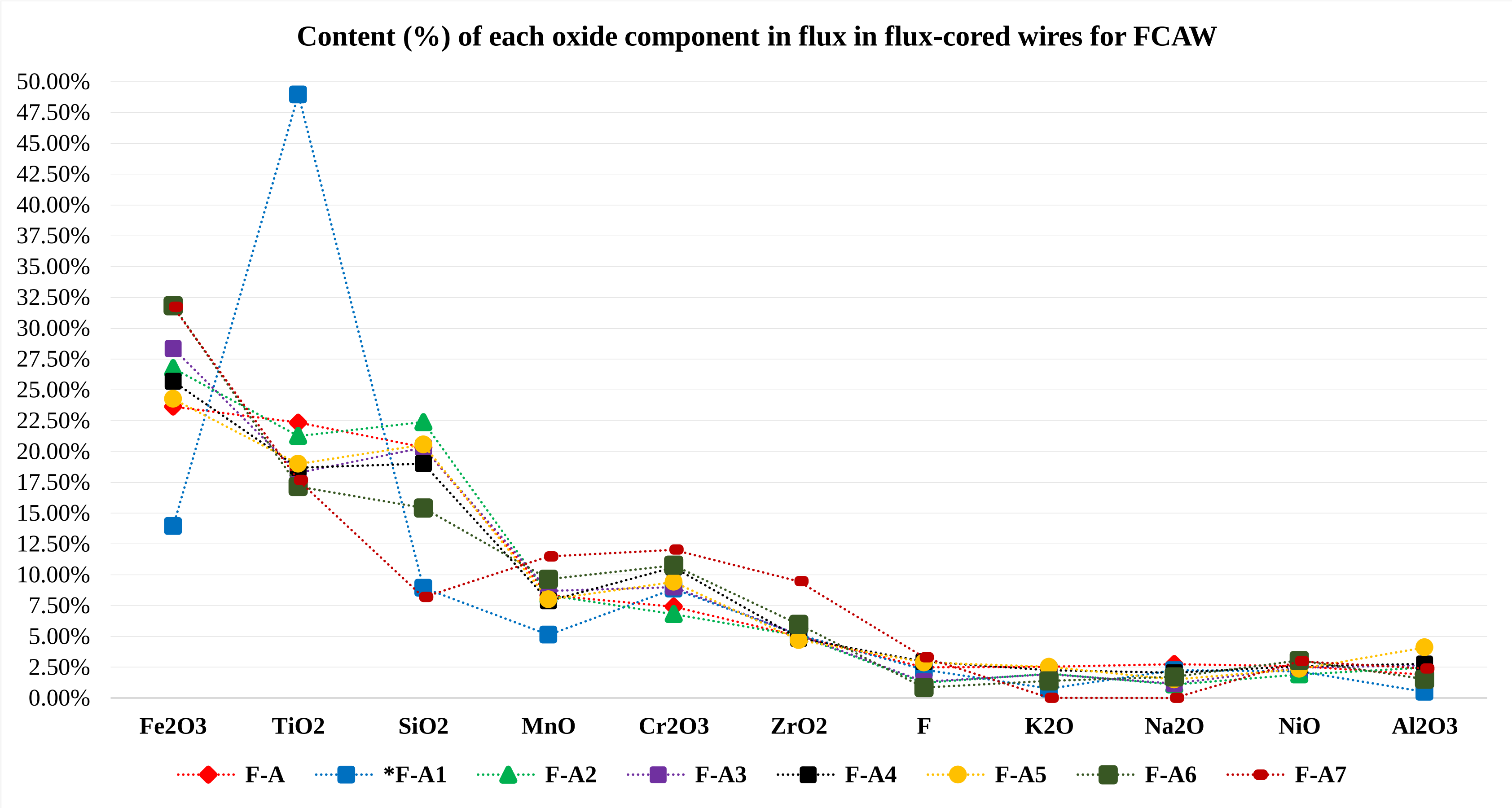


Table S 8. Pearson's correlation coefficient by each parameter in welding filler materials of nine welding rods for SMAW.

	Pearson's r	**Dependent Variables**						
Independent variables	Elements	Cr(6) in Fume	FGR per DM	FGR per WT	FGR per MU	HCGR per DM	HCGR per WT	HCGR per MU
	F	**-0.66**	**0.73**	**0.78**	**0.81**	-0.16	-0.01	0.03
	Na	0.58	**-0.61**	-0.52	**-0.73**	0.22	0.3	0.02
	K	-0.51	**0.89**	**0.83**	**0.78**	0.18	0.23	0.13
	Cr	0.55	0.04	-0.19	-0.04	**0.73**	0.49	**0.65**
	Mn	**-0.6**	0.25	0.44	0.25	-0.53	-0.31	-0.51
	Fe	0.28	-0.31	-0.2	-0.5	0.11	0.23	-0.16
	Al	0.35	0.1	0.15	-0.14	0.57	**0.68**	0.26
	Ca	-0.35	**0.81**	**0.74**	**0.76**	0.32	0.34	0.33
	Ti	-0.55	-0.14	0.08	-0.06	**-0.79**	-0.56	**-0.69**
	Si	0.34	-0.2	-0.41	-0.05	0.18	-0.13	0.35
	Pearson's r	**Dependent Variables**						
Independent variables	Oxide components	Cr(6) in Fume	FGR per DM	FGR per WT	FGR per MU	HCGR per DM	HCGR per WT	HCGR per MU
	F	**-0.61**	**0.72**	**0.71**	**0.82**	-0.11	-0.04	0.1
	Na_2O	**0.63**	**-0.73**	**-0.68**	**-0.8**	0.17	0.17	0.01
	K_2O	-0.52	**0.92**	**0.84**	**0.85**	0.19	0.21	0.2
	Cr_2O_3	0.4	0.07	-0.2	0.07	0.54	0.24	0.56
	MnO	-0.08	**0.7**	**0.66**	**0.74**	0.53	0.58	**0.63**
	Fe_2O_3	0.22	-0.41	-0.32	-0.54	-0.08	-0.03	-0.29
	Al_2O_3	0.23	0.35	0.23	0.18	**0.6**	0.51	0.4
	CaO	-0.46	**0.82**	**0.73**	**0.82**	0.16	0.15	0.25
	TiO_2	**-0.6**	-0.13	0.03	0	**-0.87**	**-0.72**	**-0.71**
	SiO_2	**0.77**	-0.16	-0.25	-0.26	**0.83**	**0.74**	**0.67**

* FGR = Fume Generation Rate, HCGR = Hexavalent Chromium Generation Rate / DM = Deposited Metal, WT = Welding Time, MU = Material Usage

Table S 9. Pearson's Correlation coefficient by each parameter in flux of eight flux-cored wires for FCAW.

	Pearson's r	**Dependent Variables**						
Independent variables	Elements	Cr 6 in Fume	FGR per DM	FGR per WT	FGR per MU	HCGR per DM	HCGR per WT	HCGR per MU
	F (%)	**-0.64**	**0.67**	**0.75**	**0.6**	-0.35	-0.4	-0.36
	Na (%)	0.57	0.47	0.49	0.4	**0.7**	**0.71**	**0.67**
	K (%)	**0.63**	0.36	0.46	0.43	**0.68**	**0.75**	**0.69**
	Cr (%)	-0.45	0.12	0.2	0.09	-0.42	-0.43	-0.42
	Mn (%)	0.01	0.11	-0.24	0.24	0.01	-0.05	0.04
	Ni (%)	0.22	0.47	0.17	0.51	0.32	0.26	0.32
	Fe (%)	0.25	-0.05	-0.31	0.1	0.15	0.14	0.18
	Al (%)	-0.03	0.21	0.39	0.33	0	0.07	0.02
	Ti (%)	-0.26	-0.21	-0.02	-0.37	-0.25	-0.25	-0.27
	Si (%)	**0.62**	0.1	0.17	0.22	0.59	**0.66**	**0.6**
	Zr (%)	-0.58	-0.03	-0.3	-0.03	-0.54	**-0.64**	-0.53
	Pearson's r	**Dependent Variables**						
Independent variables	Oxides components	Cr 6 in Fume	FGR per DM	FGR per WT	FGR per MU	HCGR per DM	HCGR per WT	HCGR per MU
	F (%)	**-0.67**	**0.64**	**0.74**	0.57	-0.39	-0.43	-0.4
	Na_2O (%)	0.56	0.45	0.47	0.38	**0.68**	**0.69**	**0.67**
	K_2O (%)	**0.64**	0.36	0.47	0.44	**0.69**	**0.76**	**0.7**
	Cr_2O_3 (%)	-0.44	0.12	0.11	0.1	-0.41	-0.44	-0.41
	MnO (%)	-0.07	0.1	-0.26	0.21	-0.06	-0.13	-0.04
	NiO (%)	0.05	0.37	0.05	0.4	0.13	0.06	0.14
	Fe_2O_3 (%)	0.16	-0.05	-0.32	0.1	0.07	0.05	0.1
	Al_2O_3 (%)	-0.06	0.21	0.39	0.33	-0.03	0.04	0
	TiO_2 (%)	-0.27	-0.21	-0.02	`0.37	-0.26	-0.26	-0.29
	SiO_2 (%)	**0.63**	0.1	0.16	0.22	0.59	**0.67**	**0.6**
	ZrO_2 (%)	-0.58	-0.02	-0.29	-0.02	-0.54	**-0.64**	-0.53

* FGR = Fume Generation Rate, HCGR = Hexavalent Chromium Generation Rate / DM = Deposited Metal, WT = Welding Time, MU = Material Usage

Table S 10. Results of multiple linear regression analysis using elements analysis result of welding filler materials in welding rods for SMAW.

	B	SE	β	P-value	VIF
Dependent Variable : Fume generation rate by welding time(mg/min)					
(Intercept)	913.60	261.28	NA	<0.05	
Si	-13.39	3.53	-1.37	<0.05	10.91
Ti	-9.42	2.71	-1.15	<0.05	9.06
Al	-27.84	12.55	-0.76	0.09	9.73
F	26.85	4.31	0.77	<0.01	1.27
Adjusted R-squared: 0.904					
F-statistic: 19.83 (p-value <0.01)					
Dependent Variable : Hexavalent chromium content in fume(%)					
(Intercept)	4.43	0.89	NA	<0.01	
Al	1.70	0.33	3.40	<0.01	20.97
Ca	-0.96	0.22	-3.57	<0.01	33.83
K	0.29	0.15	0.76	0.12	7.23
Fe	-1.37	0.30	-3.92	<0.01	36.30
Adjusted R-squared: 0.835					
F-statistic: 11.15 (p-value <0.05)					
Dependent Variable : Hexavalent chromium generation rate by welding time(mg/min)					
(Intercept)	84.42	12.56	NA	<0.05	
Si	-1.26	0.19	-5.62	<0.05	86.60
Ti	-0.64	0.10	-3.39	<0.05	35.64
Al	3.52	0.70	4.17	<0.05	62.60
Ca	-3.23	0.55	-7.10	<0.05	176.10
K	0.63	0.23	0.96	0.11	14.52
Fe	-5.90	0.93	-9.97	<0.05	295.10
Adjusted R-squared: 0.933					
F-statistic: 19.64 (p-value <0.05)					

Table S 11. Results of multiple linear regression analysis using oxides components analysis result of welding filler materials in welding rods for SMAW.

	B	SE	β	P-value	VIF
Dependent Variable : Fume generation rate by welding time(mg/min)					
(Intercept)	-1015.64	272.89	NA	0.07	
SiO_2	35.10	5.59	2.99	<0.05	42.25
TiO_2	23.97	4.03	2.95	<0.05	45.98
Al_2O_3	-83.50	18.93	-1.42	<0.05	19.27
CaO	44.34	11.44	1.77	0.06	39.08
K2O	86.77	10.49	2.45	<0.01	16.38
F	-89.03	21.63	-1.97	<0.05	42.88
Adjusted R-squared: 0.957					
F-statistic: 30.86 (p-value <0.05)					
Dependent Variable : Hexavalent chromium content in fume(%)					
(Intercept)	6.56	0.79	NA	<0.01	
TiO_2	-0.08	0.02	-0.73	<0.01	1.04
K_2O	-0.32	0.09	-0.66	0.02	1.04
Adjusted R-squared: 0.706					
F-statistic: 10.61 (p-value <0.05)					
Dependent Variable : Hexavalent chromium generation rate by welding time(mg/min)					
(Intercept)	-15.85	8.14	NA	0.15	
SiO_2	0.80	0.13	2.96	<0.01	26.68
TiO_2	0.29	0.10	1.53	0.06	29.49
Al_2O_3	-1.11	0.32	-0.82	<0.05	6.08
CaO	-0.37	0.10	-0.64	<0.05	3.26
K_2O	1.55	0.24	1.90	<0.01	9.18
Adjusted R-squared: 0.926					
F-statistic: 20.98 (p-value <0.05)					

Table S 12. Results of multiple linear regression analysis using oxides components analysis result of flux in flux-cored wires for FCAW.

	B	SE	β	P-value	VIF
Dependent Variable : Fume generation rate by welding time(mg/min)					
(Intercept)	2808.62	317.29	NA	<0.01	
SiO_2	-15.38	3.61	-0.98	<0.01	2.87
TiO_2	-26.94	4.14	-3.30	<0.01	14.08
Fe_2O_2	-47.82	6.83	-3.13	<0.01	10.92
Adjusted R-squared: 0.872					
F-statistic: 16.91 (p-value <0.01)					
Dependent Variable : Hexavalent chromium content in fume(%)					
(Intercept)	-0.15	0.17	NA	0.43	
Fe_2O_2	0.01	0.00	0.60	<0.05	1.78
Na_2O	0.14	0.03	0.89	<0.01	1.71
F	-0.07	0.02	-0.48	<0.05	1.12
Adjusted R-squared: 0.856					
F-statistic: 14.91 (p-value <0.05)					
Dependent Variable : Hexavalent chromium generation rate by welding time(mg/min)					
(Intercept)	-2.68	1.13	NA	0.08	
Fe_2O_2	0.10	0.04	0.62	<0.05	1.88
K_2O	0.32	0.21	0.32	0.20	1.70
Na_2O	0.97	0.29	0.90	<0.05	2.69
Adjusted R-squared: 0.818					
F-statistic: 11.48 (p-value <0.05)					

Table S 13. Pearson's correlation coefficients by each formula with per dependent variable using analysis result of oxides components in welding filler materials in welding rods (for SMAW) and flux-cored wires (for FCAW).

Pearson's r		Dependent Vartiables						
Independent variables	For SMAW	Cr 6 in Fume	FGR per DM	FGR per WT	FGR per MU	HCGR per DM	HCGR per WT	HCGR per MU
	(Na+K)/F	**0.64**	-0.57	-0.55	**-0.74**	0.31	0.28	0.03
	((Na+K+Li)*Cr^2)/(Si+4.7*F)	0.45	-0.05	-0.29	-0.09	0.51	0.22	0.47
	(F+K+Ca)/(Na)	**-0.67**	**0.87**	**0.84**	**0.91**	-0.07	-0.01	0.07
	(F+K+Ca+Mn)/(Na)	**-0.66**	**0.87**	**0.84**	**0.91**	-0.06	0	0.09
	(Na+Si)/(F+K+Ti)	**0.85**	-0.35	-0.44	-0.47	**0.76**	**0.63**	0.55
	(Na)/(F+K+Mn+Ti)	**0.78**	**-0.68**	**-0.67**	**-0.78**	0.4	0.36	0.19
	(Na)/(F+K)	**0.65**	**-0.81**	**-0.75**	**-0.87**	0.1	0.1	-0.05
	(Na)/(F+K+Ti)	**0.79**	**-0.66**	**-0.66**	**-0.77**	0.43	0.39	0.22
	(Cr+Mn+Al+Si)/(Ti)	**0.69**	-0.02	-0.16	-0.14	**0.85**	**0.69**	**0.67**
	(Na+Si)/(F*K)	**0.77**	**-0.79**	**-0.78**	**-0.85**	0.25	0.17	0.08
	(Na+Si)/(F*K*Ti)	**0.85**	-0.6	**-0.65**	**-0.7**	0.51	0.39	0.32
	(Na+Si)/(F*K*Ti*Mn)	0.37	**-0.86**	**-0.8**	**-0.92**	-0.33	-0.39	-0.5
	((Bi+S+Si)*Cr)/(Ti)	**0.69**	-0.07	-0.3	-0.15	**0.78**	0.52	**0.67**
Pearson's r		**Dependent Vartiables**						
Independent variables	For FCAW	Cr 6 in Fume	FGR per DM	FGR per WT	FGR per MU	HCGR per DM	HCGR per WT	HCGR per MU
	(Na+K)/F	**0.9**	-0.25	-0.39	-0.18	**0.72**	**0.76**	**0.72**
	((Na+K+Li)*Cr^2)/(Si+4.7*F)	0.59	0.09	0.21	0.07	0.53	0.59	0.52
	(F+Na+K)	0.26	**0.76**	**0.89**	**0.73**	0.5	0.52	0.49
	(F+K+Ca+Na)	0.26	**0.76**	**0.88**	**0.73**	0.5	0.52	0.49
	(Na+K+Si)/(F+Zr)	**0.72**	-0.05	0.02	0.06	**0.63**	**0.71**	**0.64**
	((Na+K+Si)*Cr^2)/(F+Zr)	0.57	0.09	0.27	0.17	0.49	0.59	0.5
	(Na+K+Si+Cr)/(F+Zr)	**0.76**	-0.09	0	0.01	**0.64**	**0.73**	**0.65**
	(Na+K+Si)/(F+Zr+Cr)	**0.66**	0.02	0.05	0.12	**0.61**	**0.67**	**0.62**
	(Na+K)/(Cr*Ti)	**0.77**	0.43	0.38	0.51	**0.84**	**0.87**	**0.84**
	(Na+K)/(Cr+Ti)	**0.76**	0.47	0.48	0.53	**0.83**	**0.88**	**0.83**
	(Na+K+Si)/(Cr+Ti+Zr)	**0.66**	0.17	0.2	0.29	**0.63**	**0.7**	**0.65**
	(Na+K+Si)/(Cr*Ti*Zr)	**0.61**	0.12	0.15	0.23	0.58	**0.65**	**0.6**

* FGR = Fume Generation Rate, HCGR = Hexavalent Chromium Generation Rate / DM = Deposited Metal, WT = Welding Time, MU = Material Usage

Table S 14. Reproducibility test result of hexavalent chromium content analysis in welding fume by filter type used for sampling welding fume.

Welding type	Product	Hexavalent chromium content(%) in welding fume			
		sample size	SD using GFF	sample size	SD using PTFE
SMAW	S-A	3	1.15	3	0.05
	S-B	3	2.51	3	0.15
	S-C	3	2.28	3	0.11
	S-A1	3	0.57	3	1.49
FCAW	F-A	3	0.19	3	0.02
	*F-A1	3	0.13	3	0.02
	F-A2	3	0.14	3	0.02
	F-A7	3	0.32	3	0.01

* SD : Standard Deviation
* GFF : Glass fiber filter
* PTFE : Polytetrafluoroethylene(hydrophobic), Teflon.

국문초록

피복아크 및 플럭스 코어드 아크 용접에서 발생하는 흄 및 6가 크롬 발생 개선을 위한 용가재 성분 연구

정선교

서울대학교 보건대학원

환경보건학과 산업보건전공

지도교수 윤충식

연구 배경: 용접 시에는 IARC 지정 Group 1 발암물질인 용접 흄과 6가 크롬이 발생하며, 선행연구에 따르면 전세계의 약 11,000만명의 근로자가 작업시간 동안 용접 흄에 노출된다 밝혀진 바 있다. 이러한 용접 흄과 6가 크롬은 용접 종류, 용접 조건, 환경영향, 용접 재료 등의 다양한 요인에 의해 발생 특성이 다르다. 많은 선행연구들을 통해서는 용접의 종류별 용접 흄 및 유해인자의 발생 특성에 대해 연구된 바 있고, 용접 전류, 전압 등의 용접 조건에 따라 용접 흄과 6가 크롬의 발생의 변화에 대해 기술한 바 있다. 하지만, 작업현장 내에서는 용접 시 용접의 성능이 가장 중요하며, 이러한 용접의 성능 유지를 위해 용접 조건을 변경하지 못하는 경우들도 더러 존재한다. 하지만, 이러한 용접 재료의 화학적 성분 함량에 따라 발암물질인 용접 흄과 6가 크롬의 발생이 어떻게 변하는 지 기술한 연구는 적다. 이에 따라, 본 연구에서는 시장 점유율이 높은 피복아크 용접과 플럭스 코어드 아크 용접을 대상으로 용접재료 성분을 달리하여 제조한 용접 재료들의 용접 시 흄 및 6가 크롬 발생량을 평가하여 통계적 추정을 통해 흄, 6가 크롬 저감에 영향을 끼치는 용가재 성분을 추정하고자 한다.

연구 방법: 자체 성능 평가 기준을 만족하는 피복아크 용접봉 9 제품, 플럭스

코어드 와이어 8 제품에 대해 용접 종류별 통일된 용접 조건 하에서 용접을 실시 후, 흄을 포집했다. 포집된 흄은 중량 분석을 통해 흄 발생량을 산출하고, IC-UV/vis로 6가 크롬 함량을, 용접 재료에 대해 XRF로 성분을 분석하였다. 용접재료 내 각 화학적 성분들의 함량, 흄 발생량, 흄 중 6가 크롬 함량 및 6가 크롬 발생량을 산출한 후, 이들의 기존 제품 대비 값의 변화에 대한 통계적으로 유의한 차이가 있는지 검정하였다. 그 뒤, 흄 발생량, 흄 중 6가 크롬 함량 및 6가 크롬 발생량을 각각 종속변수로, 용접 재료 중 특정 성분 함량을 독립변수로 상관분석을 통해 흄, 6가 크롬 발생에 영향을 끼치는 용가재 성분을 통계적으로 추정하였다. 상관분석 결과를 바탕으로, 용가재에 일정 이상의 함량으로 포함된 성분에 대해 다중회귀분석을 위한 회귀모형을 설계해 분석하였다. 마지막으로, 통계적 차이를 보인 성분들 및 선행연구들을 통해 제시된 성분들, 개별원소간 상관분석 결과와 다중회귀분석 결과들을 바탕으로 용접재료 내 성분 배합 수식을 설계해 각 종속변수와 상관분석을 진행하였다.

연구 결과: 9 종류의 피복아크 용접 제품의 용접시간당 흄 발생량은 198.0-289.3 mg/min으로 기존 대비 최대 26.7%, 평균 20%의 저감이 가능했다. 용접시간당 6가 크롬 발생량은 5.34~7.98 mg/min으로 기존 대비 최대 24.8%, 평균 3.4%의 저감이 가능했다. 8 종류의 플럭스 코어드 아크 용접 제품의 용접 시간당 흄 발생량은 590.4~821.1 mg/min으로 기존 대비 최대 23.5%, 평균 10.8% 저감이, 6가 크롬 발생량의 경우 0.34~3.31 mg/min으로 기존 대비 최대 89.7%, 평균 47.1% 발생량 저감이 가능했다. 또한, 피복아크 용접과 플럭스 코어드 아크 용접재료의 원소 함량별 흄 발생량과의 상관분석 결과, 피복아크 용접의 경우 F, K Ca, Na가 용접시간당 흄 발생량과, Cr, Ti가 용접시간당 6가 크롬 발생량과 통계적으로 유의한 수준으로 상관성을 보이는 것을 확인할 수 있었다. FCAW의 경우 F, K, Na 함량이 용접시간당 흄 발생량과, Na, K, Si, Zr, F가 용접시간당 6가 크롬 발생량과 통계적으로 유의한 상관성을 보이는 것을 확인할 수 있었다. 다중회귀분석 결과는 대부분의 회귀모형에서

독립변수 간의 간섭에 의한 다중공선성 문제가 도출되어 회귀모형의 적합도가 떨어지는 것으로 추정되었다. 이에 따라, 본 연구에서는 흄 발생량, 흄 중 6가 크롬 함량, 6가 크롬 발생량과 통계적으로 유의한 수준의 상관성을 보이는 성분 배합 수식을 피복아크 용접에 대해 11가지, 플럭스 코어드 아크 용접에 대해 10가지를 제시하였다.

결론: 종합적으로, 성분을 다르게 제조한 용접재료들에 대해 성능적 결함 없이 흄 발생량, 6가 크롬 발생량을 저감할 수 있다는 것을 증명하였다. 또한, 피복아크 용접의 경우 6가 크롬 발생량을 저감하기 위해서는 흄 발생량을 줄이는 것이, 플럭스코어드 아크 용접의 경우 6가 크롬 발생량을 줄이기 위해서는 흄 중 6가 크롬의 함량을 줄이는 것이 용이하다. 마지막으로, 용접 간 산화작용을 통해 발생되는 6가 크롬 발생을 저감하기 위해 용접 재료 제조 시 화합물들의 산화수, 전기음성도 등을 고려하여 금속 크롬 및 크롬 화합물보다 전기음성도가 높아 크롬의 산화를 억제하는 물질들로 용접재료를 제조하는 것을 권장하는 바이다. 본 연구에서 제시한 원소 함량변화에 따른 흄 발생량, 6가 크롬 발생량 식을 참고하여 흄 발생 및 6가 크롬 발생이 적은 용접 재료를 제조하여 현장에서 널리 사용된다면, 근로자의 1급 발암물질에 대한 노출 문제를 근본적으로 개선할 수 있을 것으로 기대되는 바이다.

주요어: 용접 흄, 6가 크롬, 상관분석, 피복아크 용접, 플럭스 코어드 아크 용접

학번: 2020-29645