Assessment of Welders Exposure to Carcinogen Metals from Manual Metal Arc Welding in Gas Transmission Pipelines, Iran

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Introduction

Natural gas is becoming one of the most widely used sources of energy in the world. Development of natural gas transmission network has crucial impact on the economy of gas-rich countries like Iran. The Natural Gas Industry Services include producing, moving, and selling gas. Moving gas is a very important process. It is divided into two classes: transmission and distribution. Transmission of gas means moving a large volume of gas at high pressures over long distances from a gas source to distribution centers (1, 2). Binding of the pipes is one of the most critical activities in the gas transmission, which is done with Manual Metal Arc Welding operation in Iran. Electric Arc Welding is mostly used in several major industrial processes (3). It can produce dangerous fumes (a complex mixture of gases and oxides or salts of metals) that may be hazardous to the
The welding fume generated during the welding process possesses at least 13 metals, including manganese (Mn), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), molybdenum (Mo), nickel (Ni), zinc (Zn), antimony (Sb), and vanadium (V) (5, 6). Occupational exposure to welding fumes has been associated with an increased risk of lung cancer. According to the International Agency for Research on Cancer (IARC), welding fumes are classified into group 2B (possibly carcinogenic to humans) (7). Nevertheless, nickel, cadmium, and chromium VI are three metals that were categorized as Class 1 IARC carcinogens in the early 1990s, based on sufficient evidence from experimental and epidemiological studies (8). These metals could interact directly with DNA and DNA replication, thus causing DNA damage (7, 9). In other mechanism, nickel and chromium species also stimulate cellular immune responses, while nickel and cadmium uptake can promote the release of active oxygen species (9). Chronic exposure to soluble hexavalent chromium (CrVI) result in bronchitis, asthma, ulceration and perforation of the nasal septum and liver and kidney damage in exposed workers (10). In addition, chromium (VI) compounds are Mutagenic in both prokaryotic and eukaryotic cells in vitro. Surprisingly, both chromium (III) and chromium (VI) have been refractory in producing mutagenic DNA damage in cell free systems (9). A correlation exists between increased lung cancer risk in welders and increasing length of time since first exposure to CrVI containing fumes(3).

Occupational exposure to nickel occurs predominantly in most industrial processes, particularly in welding (11). Insoluble nickel compounds are strongly carcinogenic in vitro and in vivo (9). Respiratory cancer risks are primarily related to exposure to soluble nickel and less soluble forms concentrations above 1 and 10 mg/m^3, respectively (11). Studies have showed the high concentrations of nickel in blood, tissues and in urine samples. Approximately 30% of inhaled nickel reaches the lungs, 20% of inhaled nickel is absorbed into the circulation, and Ni^{2+} has the ability to enhance DNA methylation (12). Cadmium is a naturally occurring component of the earth’s crust (13). In the occupational environments, workers may be exposed to Cd through the inhalation of fumes generated during welding of cadmium-containing materials, or inhalation of particles of metal, oxide, and pigment dust (13). Cd can cause adverse effects on multiple organs, especially on the kidney (14). The kidney is generally considered the critical organ (13). This metal can be easily absorbed into the body through the respiratory tract (14). This is because cadmium accumulates predominantly in the kidneys because of the long biological half time of 10–30 yr (15). In workers, cadmium has moreover been associated with an alteration of the lung function and has been suspected to cause lung and possibly prostate cancer. At low-level exposure, cadmium in urine (U-Cd) is considered to mainly reflect the body burden, while under high-exposure conditions and without kidney damage, it is significantly influenced by current exposure. Cadmium in blood (B-Cd) reflects mainly the last few months of exposure under moderate exposure conditions (7). The American Conference of Governmental Industrial Hygienists (ACGIH) currently sets the Biological Exposure Index (BEI) at 5 micrograms/g creatinine for workers exposed to air-borne cadmium and the World Health Organization (WHO) proposed a health-based limit of 10 nmole/mmol creatinine (10 µg/g creatinine). ACGIH currently sets a TLV of 0.01 mg/m^3 for the inhalable fraction of cadmium dust (15). Several studies showed that welders are exposed to carcinogenic metals (14, 16-18). One study has reported that the concentration of chromium and nickel in the breathing zone of welders were 140 and 50 µg/m^3, respectively; while Other study revealed that Cd values fell in range between 0.2-12.5 mg/m^3. Determination of human risk from toxic metal exposure is usually done through determining the metals in biological samples such as blood, serum, urine, hair, fingernails, and saliva (19). The aims of the this study were 1) to determine the welders
exposure to chromium, nickel and cadmium 2) to determine urinary concentration of Cr\(^{6+}\), Ni and Cd as a Biomarker 3) to find if the urine can be considered as a biomarker for evaluating the welders exposure to carcinogenic metals in gas transmission pipelines.

**Materials and Methods**

**Subjects**

In this Cross sectional study, the subjects (94 people) were selected from Iranian Gas Transmission Pipelines welders, in regions of Iran, Borujen (Chaharmahal and Bakhtiari Province), in 2011. In addition, welders work only for one shift (morn- ing shift). The task groups were Foreman, Fitter, Co-Fitter, Full pass, Filling, Filling Cap, Back Weld, and Grinder as well as 25 subjects as control group who were selected from administrative department. This department was located far from the transmission pipeline network, so personal air monitoring was not performed, and only urine specimens were collected for them. Then, subjects were classified into 3 groups according to similar tasks including welders (welding on pipes; includes Full pass, Filling, Filling Cap, n=59), Back Welders (welding inside pipes as confined space; n=6) and Assistances (working around or near of pipes; includes Foreman, Fitter, Co-Fitter, n=29). All participants in this study were male and none of them used respiratory protective devices. After obtaining approval from the Iranian Gas Engineering and Development Company (IGEDC) and informed consent from all subjects, we collected samples from breathing zone and urine of workers. Demographic data of the study population are shown in Table 1.

**Table 1:** Demographic data of welders and controls

| Group            | Variable (mean ± SD) |          |          |          |          |
|------------------|----------------------|----------|----------|----------|----------|
|                  | Age (yr)*            | Height (cm) | Weight (kg) | Working History (yr) * | Smokers (n) |
| Welders (N=94)   | 27.45±6.51           | 176.50±6.43 | 75.39±10.05 | 5.09±3.71 | 44        |
| Controls (N=25)  | 34.16±10.24          | 171.60±20.07 | 75.36±11.91 | 3.52±2.04 | 5         |

*: statistically significant (P<0.05).

**Air Monitoring**

Total chromium, nickel and cadmium samples were collected according to U.S.A National Institute of Occupational Safety and Health (NIOSH) Method 7300, while NIOSH Method 7600, developed primarily for measuring Chromic acid concentration, was used to determine the Cr\(^{6+}\) concentrations (20,21). In case of Cr, Ni and Cd, each sampling train consisted of either a closed-face 25 mm polystyrene filter cassette. Each cassette, containing a 0.8 µm pore size Mixed Ester Cellulose (MCE), was connected to a personal sampling pump (Model 224-PCXR3; SKC, Bland ford Forum, UK), which calibrated at flow rate of 2.0 ± 0.1 L/min. For Cr\(^{6+}\) sampling, PVC filters with diameter of 37 mm and pore size of 5 µm were used.

Workers exposure to welding fumes was measured gravimetrically. The MCE filters weighed using the balance (model: Sartorius CP 225D, Germany) before and after air sampling. In all cases, the filters were put in desiccators for 24 hours before weighting (16, 22). In addition, all samples were taken during the work shift (8 hours).

For the determination of Cr, Ni and Cd, MCE filters were extracted, using digestion with HNO3 and then analyzed by ICP-AES (model: Spectro Arcos OES EOP), while Cr\(^{6+}\) samples were analyzed, using UV-Vis spectrophotometer (model M501, company Camspec) at wavelength of 540 nm (20, 21).

**Biological Monitoring**

Ninety four case group urine samples as well as 25 control ones were collected in PVC bottles during the entire work shift (8 hours) HNO3 was added to samples as a preservative (7). All bottles were
were soaked overnight in 30% (v/v) Nitric Acid, thoroughly rinsed with Deionized Water and dried. After sampling, all urine specimens were stored at a –70°C in a refrigerator before analysis (23). The urinary metals were analyzed, using Atomic Absorption Spectrometry (AAS) with a graphite furnace (GBC, Model 932, made of Austria) after microwave digestion.
To minimize the effect of the various hydration states of the workers, the urinary metals concentrations were further calibrated by their creatinine concentrations and thus were expressed in terms of µg/g creatinine (24). The creatinine concentration was analyzed according to a routine colorimetric procedure, in a medical diagnostic laboratory.

Data Analysis
The data were processed, using SPSS version 17 and Microsoft office excel 2010. The statistical methods included Student’s t-test and ANOVA test. A level of P<0.05 was considered statistically significant. In addition, Partial correlation analysis was used to determine the correlation among urine metals levels and airborne metals concentrations.

Results
Subjects’ exposure to fumes and its carcinogenic metal content is shown in Table 2.

| Contaminant                  | Group          | N0. of sampling | Mean±SD (mg/m³) | Comparison Between Groups (ANOVA Test) | Multiple Comparison (Bonferroni Test) | Comparison with TLV (one sample t Test) |
|-----------------------------|----------------|-----------------|-----------------|---------------------------------------|--------------------------------------|----------------------------------------|
| Total fume (TLV: 5)         | Welders        | 59              | 11.16±3.922     | P<0.001                               | Welders-Back Welders                 | t = 12.06, P<0.001                      |
|                             | Back Welders   | 6               | 21.51±8.722     |                                       | Back Welders-Welders-                 | t = 4.16, P=0.049                       |
|                             | Assistances    | 29              | 2.754±2.040     |                                       | Assistances-Back Welders              | t = -3.977, P<0.001                     |
| Hexavalent Chromium (TLV: 0.01) | Welders       | 59              | 0.00200±0.001   | P=0.002                               | Welders-Back Welders                 | t = -38.339, P<0.001                    |
|                             | Back Welders   | 3               | 0.00501±0.002   |                                       | Welders-Back Welders                 | t = -7.37, P=0.018                      |
|                             | Assistances    | 29              | 0.00085±0.000   |                                       | Assistances-Back Welders              | t = -45.199, P<0.001                    |
| Total Chromium (TLV: -)     | Welders        | 59              | 0.01954±0.006   | P<0.001                               | Welders-Back Welders                 | -                                      |
|                             | Back Welders   | 3               | 0.04567±0.012   |                                       | Back Welders-Back Welders            | -                                      |
|                             | Assistances    | 29              | 0.00936±0.007   |                                       | Assistances-Back Welders              | -                                      |
| Cadmium (TLV: 0.01)         | Welders        | 59              | 0.0018627±0.00 | P<0.001                               | Welders-Back Welders                 | t = -139.64, P<0.001                    |
|                             | Back Welders   | 3               | 0.0026014±0.00  |                                       | Back Welders-Back Welders            | t = -7.93, P=0.016                      |
|                             | Assistances    | 29              | 0.0010104±0.00  |                                       | Assistances-Back Welders              | t = -47.163, P<0.001                    |
| Nickel (TLV: 0.1)           | Welders        | 59              | 0.08252±0.127   | P=0.08                                | Welders-Back Welders                 | t = -1.049, P=0.298                     |
|                             | Back Welders   | 3               | 0.23260±0.068   |                                       | Back Welders-Back Welders            | t = 0.820, P=0.498                      |
The results showed that Back Welders and Assistances groups had maximum and minimum exposure to total fume and its containing elements, respectively. ANOVA test results showed that there were significant differences among tasks groups in terms of exposure with total fume and elements except nickel. Subsequently, Bonferroni test (Multiple Comparison) confirmed that there are significant differences between Welders – Back Welders groups exposure to total fume and chromium, while in comparison of Welders and Back Welders with Assistances group, the differences were seen for total fume and elements except Ni.

The results also showed that the mean concentration of total fume and Ni were higher than TLV for Back Welders group; while hexavalent chromium and Cd were lower than it was. In addition, results showed that exposure of Assistances group to total fume and metals were lower than TLV (22).

The proportions of Cr$^{6+}$ in total Cr were 0.102, 0.109 and 0.091 for welders, Back Weld and Assistances groups, respectively.

Totally, Comparison of mean concentrations of 94 samples, total fume and its containing metals, ( total fume: $9.097\pm6.336$, Cr$^{6+}$: $0.0019\pm0.0017$, Cd: $0.0021\pm0.0019$, Ni: $0.082\pm0.067$ mg/m$^3$) with the related TLVs showed that only total fume was higher than TLV but Ni, Cr$^{6+}$ and Cd were much lower than TLVs (Fig. 1).
Fig. 1: Concentration of total fume and its elements with their TLV. A: total fume, B: hexavalent chromium, C: cadmium and D: nickel

Urinary concentration of Cr\textsuperscript{VI}, Cd and Ni in case and control groups are presented in Table 3. Among the case groups, Back Welders and Assistances groups had maximum and minimum urinary concentrations, respectively. Although the concentrations of the three metals in the urine of case group were higher than those of control group were, only the differences were significant for Welders and Back Welders.

Table 3: Urinary concentration of carcinogenic metals

| Metal                | Group             | No. of sampling | Mean±SD   | Minimum | Maximum | Comparison                  |
|----------------------|-------------------|-----------------|-----------|---------|---------|----------------------------|
| Chromium, µg/lit     | Welders           | 59              | 6.37±3.74 | 1.000   | 18.000  | Welders-Control: \(p=0.001\) Back Welders –Control: \(p=0.001\) |
|                     | Back welders      | 6               | 12.67±4.50| 6.000   | 17.000  |                           |
|                     | Assistances       | 29              | 1.98±1.05 | 1.000   | 4.800   | Assistances-Control: NS    |
|                     | Control           | 25              | 1.04±0.56 | 0.000   | 1.900   |                           |
| Cadmium, µg/g creatinine | Welders      | 59              | 0.50±0.53 | 0.00    | 1.85    | Welders-Control: \(p=0.004\) Back Welders –Control: \(p<0.001\) |
|                     | Back welders      | 6               | 1.72±0.65 | 1.18    | 2.41    |                           |
|                     | Assistances       | 29              | 0.16±0.22 | 0.00    | 0.73    | Assistances-Control: NS    |
|                     | Control           | 25              | 0.04±0.07 | 0.00    | 0.28    |                           |
| Nickel, µg/Lit       | Welders           | 59              | 4.75±4.56 | 1.00    | 24.00   | Welders-Control: \(p=0.001\) Back Welders –Control: \(p<0.001\) |
|                     | Back welders      | 6               | 11.46±6.64| 4.60    | 22.00   |                           |
|                     | Assistances       | 29              | 1.39±1.09 | 0.05    | 4.60    | Assistances-Control: NS    |
|                     | Control           | 25              | 0.32±0.29 | 0.00    | 0.90    |                           |

NS: not statistically significant

Correlations between airborne and urinary concentrations for three metals were investigated using Partial correlation analysis. Results showed that Partial correlation coefficients ranged 0.296-0.481 (Table 4), so there was a weak direct relationship between workers exposure to carcinogenic metals and their urinary concentrations in Gas Transmission Pipelines workers.

Table4: Partial Correlation* between welders exposure to metals and their urinary amounts

| Metal                | Concentration of metal in breathing zone (mg/m\(^3\)) | Concentration of metal in urine | Partial Correlation | Statically analysis | Correlation |
|----------------------|------------------------------------------------------|--------------------------------|---------------------|---------------------|-------------|
| Chromium             | 0.0209839                                            | 5.82835 (µg/Lit)               | 0.481               | \(p<0.05\)        | YES         |
| Cadmium              | 0.0021383                                            | 0.5080 (µg/gr creatinine)      | 0.296               | \(p<0.05\)        | YES         |

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Discussion

The adverse health effects of occupational exposure to welding fumes have been studied by researchers (7, 14, 25-27). Welders are frequently exposed to fumes containing carcinogenic metals (chromium, cadmium and nickel) generated by Manual Arc Welding (6, 14, 16, 28, 29).

In the current study, mean concentrations of total fumes generated by MMA welding were obtained in the range of 2.75-11.16 mg/m$^3$ which were higher than the amounts (2.7 mg/m$^3$) reported earlier (16). However, total chromium, hexavalent chromium and nickel concentrations were lower than that of what they reported. These differences may be due to base metal and electrode types used in these two studies.

During regular MMA welding low amounts of Cr$^{6+}$ were found, which is in agreement with previous results (16, 28). The Cr$^{6+}$/Cr ratio in fume samples during regular MMA welding was lower than that of the samples collected in previous studies (10, 29, 30). As mentioned above, cause of lower levels could be due to the base metal types used in this study. In our study, base metal was iron, while in previous studies, was steel. Based on the literature, MMA welding operation on Stainless Steel produces higher chromium in comparison with same operation on Iron sheet (31).

There was high prevalence of neurological disorders in welder’s exposure to cadmium as a component of welding fumes (14). In addition, Xianliang Wang reported amounts of cadmium in breathing zone of welders 0.17 (0.1-3) mg/m$^3$. In the current study, Back Weld group has maximum exposure to cadmium (0.0026014±0.00161 mg/m$^3$), however, it is lower than findings of previous study. Therefore, it seems that the potential probability of neurologic effects due to cadmium exposure could be negligible in welders of Gas Transmission Pipelines.

The results indicated that exposure of back welders to nickel was in agreement with the findings of Mansouri N. et al. and Karlsen et al. (16, 32). Other groups’ exposure to nickel was in compatible with Karlsen et al. (19).

Totally, results of current investigation indicated that Back Welders had maximum exposure to fumes and its elements. This is due to inappropriate working conditions including welding in confined space with poor ventilation. In confined spaces without enough ventilation, welding can be deadly (33). It has been calculated that working in a confined space is 150 times more dangerous than doing the same job outside (34). Thus, more attention should be paid to the working conditions of Back Welders group.

Urine samples, as recommended biological media (19) were selected to detect the subjects’ exposure to Cr, Cd and Ni. The results of this study were in accordance to previous studies (10, 12, 15). In addition, it showed that two task groups of Back Welders and welders have a significantly higher level of metals (Cr, Cd and Ni) in comparison to control group. Urinary concentrations of three metals including Cr, Cd and Ni among subjects (n=94) were about 4.5, 12 and 14-fold greater than those detected in controls, respectively. Such a result was expectable. Because, the more the exposure of welders to fume and its elements, the more material accumulation at their bodies.

Our results showed that metals’ concentrations in urine of all task groups were lower than BEIs, except urinary chromium concentration in Back Weld group (12.67 vs. 10 µg/L) (24). This increment could be related to working condition of back weld group in confined space, giving higher exposure to airborne chromium in comparison with other groups.

Urinary metals (U-Cr, U-Cd and U-Ni) concentrations in the exposed groups in our study were compared with the results reported in other studies (4, 5, 6, 30). This comparison showed that some of the previous studies reported higher U-metals concentrations than our study and some lower. The reasons for such a difference may be

\[
\begin{array}{cccc}
\text{Nickel} & 0.0827490 & 4.5291 \text{ (µg/Lit)} & 0.315 & P<0.05 & YES
\end{array}
\]

*Adjusted for age, working history, and smoking. Statistical significance will be observed if $P < 0.05$. 

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due to: a) The type and quantity of fumes are influenced by various welding factors including arc current, arc voltage, welding types, type of electrode, base metal, etc (18, 35). b) On the other hand, the amount deposited and particle solubility, surface area, and size are factors that will affect the behavior of metal fumes deposited in the respiratory system and will probably account for the differences in retention and clearance via absorption (12).

However, few investigations have focused on determining the relationship between airborne and urinary concentrations of Cr, Cd and Ni in welders. Only in one study (10), it was found significant relationship \[ \text{CURINE} = 1.86 \times \text{CINH} - 0.21 \] (\(R^2=0.87\)) between inhalable Cr\(^{\text{IV}}\) and urinary chromium concentrations. They suggest that the inhalable aerosol sampling results were able to explain the variation in workers’ urinary chromium concentrations up to 87\%.

While in the case of other metals such as manganese, dozens of studies investigated correlation between airborne and urinary concentration of manganese (36-39). Results of previous studies (36, 39) showed that there was significant correlation between airborne and urinary concentration of manganese.

Significant correlations were obtained between airborne and urinary concentrations of three metals, but there were low Correlation coefficients between them \[ \text{CURINE} = 228.1 \times \text{CINH} + 1.43 \] (\(R^2=0.481\)), \[ \text{CURINE} = 112.5 \times \text{CINH} + 0.325 \] (\(R^2=0.296\)) and \[ \text{CURINE} = 35.56 \times \text{CINH} + 1.375 \] (\(R^2=0.315\)), respectively. Regarding to our results, we cannot use the results of airborne concentrations in estimation urinary concentrations for three metals of chromium, cadmium, and nickel and vice versa. Thus, we concluded that urinary metals are not reliable biomarkers for exposure assessment of Gas Transmission Pipelines welders to these metals. The weak correlation between air and urine samples could be due to: Physiological makeup and health status of the worker, such as body build, diet(water and fat intake) metabolism; Occupational exposure factors such as community and home air pollutants, water and food component, smoking, alcohol and drug intake; Methodological factors including specimen contamination or determination during collection and storage and bias of selected analytical method; Location of the air monitoring device in relation to the workers breathing zone; Particle size distribution and bioavailability; Variable effectiveness of personal protective devices (24).

In summary, our results indicate that Back Welders group had high exposure to fumes and its elements in comparison with Welders and Assistances. Thus, we suggest that more attention should be paid to the working conditions of Back Weld group, specifically providing proper ventilation and protective personal devices. Weak relationships were found between airborne and urinary concentrations of three metals (Cr, Cd and Ni). Then we concluded that the urinary metals concentration is not recommended as a Biomarker for assessment of welders’ exposure who works in outdoor situation.

**Ethical considerations**

Ethical issues (Including plagiarism, Informed Consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc) have been completely observed by the authors.

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