Occupational Exposure to Cr (VI) during Furnace Maintenance Activities in Colombian Cement Plants

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Abstract

Hexavalent chromium is a confirmed carcinogenic agent in humans, present in different industrial processes, including cement production industry, this cross-sectional study describes the occupational exposure to hexavalent chromium in a cement plant during maintenance process of the principal furnace. 16 personal full-shift random samples in 2 Similar Exposure Groups were taken and statistical estimators were compared with Cr (VI) ACGIH TLV-TWA adjusted by Brief & Scala based different work schedules. Results indicate that this kind of activities represent a major risk of exposure to Cr (VI) for workers, statistical estimators warn that based on the technology used on maintenance process exist differences on worst case scenario estimators but maintain central tendency similar.

Problem

Cement-producing plants are a potential source of atmospheric chromium, with an estimated chromium of 41.2 mg/kg in Portland cement, with soluble chromium of 4.1 mg/kg of which 2.9 mg/kg is Cr (VI) (0.03 - 7.8 mg / kg). Chrome in the cement comes from 1) raw materials or fuel, 2) furnace lining built with refractory bricks (magnesium-chromium) 3) deterioration of the metal in the grinding process 4) additions of gypsum, pozzolan, high-level slag granulated kiln and cement kiln powder. In Colombia, based on Carcinogenic Exposure (CAREX), it was estimated that 52,654 are exposed to Cr (VI) and compounds, this being the fifteenth carcinogenic agent with the highest estimated percentage of exposed workers in Colombia. Chromium in its non-toxic trivalent oxidation state is present in the raw materials (clay, lime, or mineral) used for the production of cement. In the Clinker formation process, the temperature of the material in the furnace ranges from 1,400 to 1,500ºC corresponding to flame temperatures of around 2,000ºC. The clinkerization reaction is carried out under oxidizing conditions, therefore, an excess of air is required in the sintering zone of the furnace, which allows trivalent chromium to oxidize in reactive hexavalent form. Worst-case scenario for workers occur during the kiln maintenance procedures, considering that it corresponds to the activity that involves closer contact with dispersed materials with Cr(VI) content.

Objective

Determine occupational exposure to Cr (VI) during cement furnace maintenance processes in 2 Colombian production plants.

Methods

16 full-shift personal air samples of Cr (VI) random sampled in 2 Cement Plants during furnace maintenance process.

- Basic Characterization to conform Similar Exposure Groups (considering Process, Tasks & Positions) based on recommendations included on Chapter 3 & 4 of "A Strategy for Assessing and Managing Occupational Exposures", 4th edition AIHA.
- Sample strategy involves random sampling in 2 Similar Exposure Groups per each plant, considering furnace technologies and maintenance process involved.
- Samples performed according to OSHA ID215v2 IC-UV (Ion Chromatography Ultraviolet Detection), analyzed in AIHA accredited laboratory.
- Statistical analysis, were performed in the software LogNorm2® Version 2.9 for Windows & AIHA IHSTAT+ v.235 Dec 2013.
- Results were compared with ACGIH Hexavalent Chromium TLV-TWA and it was adjusted with Brief and Scala Model considering work shift differences.

Results

Compliance-Based Analysis

Based on individual results in comparison with the reference value applicable to Hexavalent Chromium (0.16 ug/m3), it is possible to establish that:

- 75% (12) personal full-shift samples were above TLV-TWA B&S
- 25% (4), presented concentrations that exceeded the action value.
- Minimum Value Unbiased Estimator, presented central tendency magnitudes close to 0.6 ug/m3, estimator that was found between a Lower Confidence Limit (LCL) of 0.4 ug/m3 and an Upper Confidence Limit (UCL) of 1.3 ug/m3.
- It can be inferred that the results, independent of having been carried out in independent scenarios, maintain some degree of homogeneity taking into account the geometric standard deviation of the Log Normal distribution of 2.62.

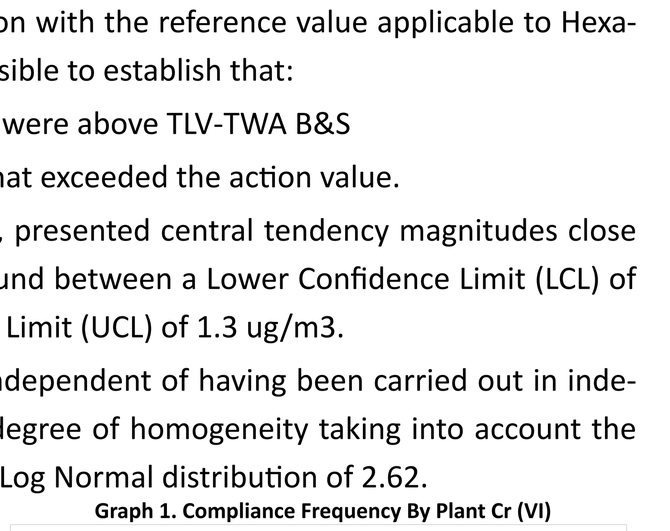
Very High Risk
TWA≥ 10 X TLV-TWA
Hight Risk
TWA ≥ TLV-TWA < 10 X TLV-TWA
Moderate-High Risk
TWA ≥ 50% TLV-TWA < TLV-TWA
Moderate-Low Risk
TWA ≥ 10% TLV-TWA < 50% TLV-TWA
Low Risk
TWA < 10% TLV-TWA
Incipient Risk
TWA < LOQ

Graph 1. Compliance Frequency By Plant Cr (VI)

Table 2. Statistical Results Cr (VI) Samples

TLV-TWA B&S	0.16 ug/m3
Proportion (p)	0.95
Confidence (c)	0.95
Number of Samples (n)	16
Mean (MVUE)	0.65 ug/m3
LCL	0.43 ug/m3
UCL	1.36 ug/m3
Geometric Mean	0.41 ug/m3
Geometric Standard Deviation	2.74 ug/m3
X(95%)	2.13 ug/m3

Graph 2. CDF Plot Cement Plant Maintenance Process Cr (VI)



Basic Characterization Analysis

2 Similar Exposure Groups were conformed in order to identify if the variables associated with different exposure circumstances and working conditions could explain changes in potential exposure patterns. The furnace maintenance processes in major shutdowns predominantly involve the breaking of the crust and replacement of refractory bricks, working conditions that were reproduced in both exposure scenarios; the existing differences involved maintenance times, occupationally exposed personnel and fracturing technologies by means of semi-automatic or manually operated pneumatic drills, as well as the typology of refractory linings and the differences in the characteristics of the cement produced in each plant.

SEG Analysis

In the case of Exposure Group Similar A (SEG A), fracture and removal technologies were used with semi-automatic drills with remote operation, in this case 10 full-shift personal samples were taken. According to the analysis of the goodness-of-fit test Log-Normal-Distribution is recommended (0.9197> 0.9168) considering Shapiro-Wilk test. The MVUE compared to the adjusted occupational exposure limit allowed establishing that the permissible limit is exceeded 4 times and, based on the Percentile .95, the exposure could be exceeded more than 12 times considering the estimated worst-case scenario. According to the values calculated with a confidence level of 95%, the exposures exceed the exposure limit at least 94.98% of the contemplated exposure scenarios, finally, the exceeding fraction with respect to the lower confidence limit was 63.60%.

Based on the statistical results applicable to 6 full-shift samples in the GES B that carried out drilling and dismantling activities of the refractory brick on the neck of the kiln outlet and functions of removal and disposal of waste with pneumatic drill, it was recommended a Log Normal distribution over a normal distribution (0.9062> 0.7999), the unbiased estimator of minimum variance presented values that exceeded the reference standard more than 4 times, with an estimated worst case condition associated with the .95 percentile that exceeds more than 16 times the adjusted limit.

In comparison, the SEGs under observation show similarities in relation to the average of exposure, since the values associated with MVUE presented equivalent values. Subtle differences were found in relation to the most favorable case of exposure associated with the lower confidence limit with a difference of 0.1 ug/m3 between GES A and GES B and significant differences between the condition of higher probable risk, associating the upper confidence limit between GES A 1.7 ug/m3 versus GES B 9.99 ug/m3.

Table 2. Statistical Results By SEG

	SEG A	SEG B
TLV-TWA B&S	0.16 ug/m3	0.16 ug/m3
Proportion (p)	0.95	0.95
Confidence (c)	0.95	0.95
Number of Samples (n)	10	6
Mean (MVUE)	0.64 ug/m3	0.62 ug/m3
LCL	0.40 ug/m3	0.31 ug/m3
UCL	1.70 ug/m3	9.99 ug/m3
Geometric Mean	0.44 ug/m3	0.35 ug/m3
Geometric Standard Deviation	2.54 ug/m3	3.33 ug/m3
X(95%)	2.04 ug/m3	2.57 ug/m3

Discussion

The average magnitude of the exposures of workers linked to both strata did not show major differences, allowing us to establish that the use of semi-automatic remote devices reduces the maximum magnitudes of workers, considering that there were no significant differences between the intergroup geometric standard deviations.

The fractions of exceedance with respect to the lower confidence limits in the GES, also presented significant differences with a proportion close to 10% in the most favorable case of potential exposure, however, both were found above 50%, allowing to establish that In the case of the lowest potential risk, there is a probability greater than 50% of exceeding the adjusted occupational exposure limit.

Conclusions

According to Bodaghpour et al (2012), the chromium in the cement comes from the kiln with magnesium-chromium bricks and the conditions in the kiln itself, which include a high amount of calcium oxide (CaO), free lime and favorable alkalis for oxidation of Cr to Cr (VI) and additions of gypsum, pozzolan and granulated blast furnace slag with kiln dust. In this sense, the maintenance of the furnaces makes it possible to maintain a product without exceeding 2 ppm of Cr (VI), and thus avoid the effects produced by Cr (VI) on the health of the population that uses the cement or the preparations to cement base.

The magnitudes found warn that furnace maintenance activities in cement plants represent a potential risk for workers to Hexavalent Chromium, however, it should be noted that these are non-routine work activities, which do not necessarily reflect the long dose term of workers linked to work activities, unless they are carried out continuously by workers specialized in this type of task.

The impact on the implementation of engineering controls in the estimated maximum magnitudes is evident, with which said controls must be reinforced to mitigate the potential risk. It is also necessary to emphasize surveillance measures in health and personal respiratory protection to reduce the probability of respiratory and dermal impact.

It is necessary to delve into these types of studies to offer an overview of other scenarios of potential exposure to Hexavalent Chromium in activities that involve the production and uses of cement.

Acknowledgments

Acknowledgments to the companies that participated in this study, to the Occupational Hygienists of our country for their valuable contributions in the construction of the science and the art of Occupational Hygiene in Colombia .

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