

Release of volatile chromium species from stainless steel and subsequent interaction with insulating wool products

Introduction

This ECFIA Information Sheet details current knowledge on the emission of volatile chromium (Cr) species from stainless steel at elevated temperatures and subsequent deposition on media with high surface area. The use of insulating materials in contact with stainless steel is a common application and concerns have been raised about potential hexavalent chromium (Cr(VI)) deposition. ECFIA, in partnership with Montana State University, have reviewed available literature and performed a series of experiments looking at hexavalent chromium deposition, the findings are detailed herein.

Stainless Steel and Chromium Release

The emission of volatile chromium species from chromia-forming stainless steels at elevated temperatures is of concern due to the carcinogenic nature of hexavalent chromium (Cr(VI)). In terms of stainless steel, a brief overview of the following is described:

- The source of Cr species including Cr(VI);
- The reactive evaporation of Cr species from stainless steels; and,
- The interaction or deposition of Cr species on glass and ceramic materials.

This is general guidance only. The actual chromium volatilisation rate is dependent on not only the grade and finish of stainless steel but also the temperature and atmosphere conditions. Please refer specific questions to the stainless-steel manufacturer.

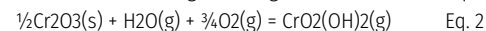
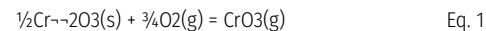
Source of Chromium Species

The source of Cr species from corrosion resistant alloyed steels (e.g., stainless steel) is commonly found in the thin chromia-based protective surface layer. The corrosion resistance in various grades of ferritic and austenitic stainless steel is often achieved by the addition of critical amounts of chromium, nickel and other minor additives. The addition of chromium to steel, results in the formation of a very thin but impermeable layer of chromium oxide (chromia) on the surface of the material, which, at low temperatures, acts as a passive protective film and prevents further oxidation of the material, thus giving it corrosion resistance [1].

Chemical reactions causing the release of Chromium from Stainless Steel

Chromium volatility, or the reactive evaporation of chromium from chromium containing oxides, such as the passive protective layer of chromia found on the surface of stainless steel, is a well-documented phenomenon, with hexavalent Cr species forming both in dry and moist oxidizing conditions [2].

The reactive evaporation of Cr from chromia occurs in atmospheres of oxygen, forming CrO₃(g) (eq. 1), and increases in the presence of water vapor, forming CrO₂(OH)₂(g) (eq. 2) [3-5]: Both reaction products are hexavalent chromium species and are well known carcinogens.



Experiments (published by N Jacobson, C Gindorf & G. Tatar [4-6]) have shown that exposure to elevated temperature in an oxidising atmosphere (with or without moisture) is sufficient to cause the formation of volatile chromium species from stainless steel. The chromium volatilisation rate from the surface of stainless steel is also shown to be affected by the heat treatment temperature [5]. The onset temperature for chromium volatilisation varies between different grades of stainless steel but typically is in the 500-550°C range.

Interaction or deposition of Chromium on glass and ceramic materials

The level of chromium vaporised from stainless steel is not believed to be affected by any refractory insulation material that is situated in contact with or proximity to stainless steel. The published literature uses different experimental designs with the collector material either in direct contact with the stainless steel, or downstream and separate from the stainless steel as seen in Figure 1. This design is also used when assessing deposition using a pure chromia source to optimise volatile chrome production. The amount of chromium species deposited on such material's surfaces, is shown to be affected by its chemistry and surface area.

Figure 1 below presents the experimental setup used in above mentioned studies, as shown in the figure, the stainless steel or chromia powder is heat treated inside a tube furnace with no physical contact to the fibrous collector material which is situated outside the furnace to collect the volatile chromium species.

Several fibrous materials including quartz wool, aluminosilicate wools (e.g., refractory ceramic fibre (RCF)), alkaline earth silicate wools and polycrystalline wools have been used in these studies in a similar experimental setup, to study the interaction of fibrous materials with volatile chromium species released by stainless steel. The level of chromium collected, including Cr(VI), was found to be affected by the chemistry and surface area of the fibrous material.

Further work was carried out using chromia powder to investigate claims in the industry that pure silica fibres did not collect Cr(VI) from volatilised chrome species. Several commercially available products were obtained by Montana State University, one from Europe (Insulation 1), one from Australia (Insulation 2) and one from their normal laboratory source of "quartz" wool.

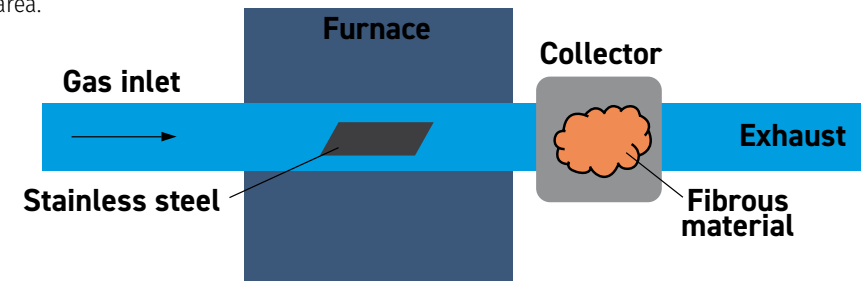


Figure 1 – Experimental setup used to study the interaction of fibrous insulation materials with volatile chromium species released from stainless steel at high temperature [2-5]

These samples were tested downstream from chromia powder at 3 levels of humidity, “bone-dry” 0% water, “normal” 3% humidity and “high” 10% humidity. These tests showed increasing Cr (VI) deposition as humidity increased; with differences between the insulation materials indicating that chemistry or surface area has some impact on deposition rates. Highlighted in figure 2 and table 2 below are the results for normal humidity, demonstrating Cr (VI) formation on all three samples when analysed by ICP-MS and DPC visual or spectroscopic colorimetry. There is also visible discolouration of the fibre samples again indicating the presence of Cr (VI) species.

Available Data on Low Biopersistent fibre

There is very limited experimental data available concerning the interaction of volatile chromium species with low biopersistent (LBP) fibre. As mentioned previously the amount of volatile chromium species generated can vary dependant on grade and finish of stainless steel as well as heat treatment conditions including temperature and atmosphere. These conditions are believed to have more bearing on the amount of volatile chromium formed and hence collected by various fibrous insulating materials, more so than the chemistry of said fibrous materials.

There is also no evidence in published literature or experiments conducted that any insulation material promotes the formation of hexavalent chromium from stainless steel.

Discussion and Conclusion

ECFIA, representing the HTIW industry, has obtained independent verification that the reactive evaporation of Cr (VI) from stainless steels is not catalysed by the presence of insulation materials. Furthermore, it has been demonstrated that any high surface area material can act as collector of Cr (VI) species when they are downstream from stainless steel or other chromia sources that have been exposed to high temperatures. The amount of Cr (VI) evaporated from stainless steels is influenced by humidity of the air, type of stainless steel, and the temperatures, and its downstream condensation/deposition is ubiquitous on all insulation products investigated. Insulation product chemistry and morphology may have implications on collection efficiency and speciation of the Cr(VI) deposited, but not on the quantity of Cr(VI) evaporated from the stainless steel.

This information sheet deals with the scientific principles behind Cr(VI) formation and deposition at elevated temperature. It should be noted that appropriate measures and risk assessments should be taken when handling stainless steel and contacting/downstream insulation materials that have been exposed to high temperature corrosive environments.

Note: This publication is for information only and does not claim to be comprehensive and ECFIA shall not incur any liability for its use. For more information on the subjects mentioned in this issue, please contact ECFIA (3 rue du colonel Moll, 75017 Paris) or connect to its website: www.ecfia.eu

References

[1] Olsson, C.O. and Landolt, D., 2003. Passive films on stainless steels - chemistry, structure and growth. *Electrochimica acta*, 48(9), pp.1093-1104.
 [2] Tatar, G., Gannon, P., Swain, N., Mason, R., Remington, E. and Dansereau, S., 2019. Investigation of surface interactions between volatile chromium species and ceramics. *Surface and Interface Analysis*, 51(5), pp.506-515.
 [3] E. J. Opila, D. L. Myers, N. S. Jacobson, I. M. B. Nielsen, D. F. Johnson, J. K. Olminsky, and M. D. Allendorf, *Journal of Physical Chemistry*, 111, 1971-1980 (2007).
 [4] N. Jacobson, D. Myers, E. Opila, and E. Copland, *Journal of Physics and Chemistry of Solids*, 66 (2), 471-478 (2005).
 [5] C. Gindorf, L. Singheiser, and K. Hilpert, *Journal of Physics and Chemistry of Solids*, 66 (2), 384-387 (2005).
 [6] Tatar, G., Gannon, P., Swain, N., Mason, R., Remington, E. and Dansereau, S., 2018. XPS Characterization of Aluminosilicate Fibers Post Interaction with Chromium Oxyhydroxide at 100–230° C. *Journal of The Electrochemical Society*, 165(10), pp.C624-C632.
 [7] Key, C., Eziashi, J., Froitzheim, J., Amendola, R., Smith, R. and Gannon, P., 2014. Methods to quantify reactive chromium vaporization from solid oxide fuel cell interconnects. *Journal of The Electrochemical Society*, 161(9), pp.C373-C381.
 [8] Young, D.J. and Pint, B.A., 2006. Chromium volatilization rates from Cr2O3 scales into flowing gases containing water vapor. *Oxidation of Metals*, 66(3-4), pp.137-153.

Table I. Information on the insulating fibres.

	QUARTZ WOOL	INSULATION #1	INSULATION #2
Fiber Diameter, µm (Avg, Std Dev)	21.45, 14.30	9.36, 2.06	10.65, 1.29
EDX Chem. Analysis (Oxygen Balance)	Si (46.3 wt%), S (0.5 wt%), and Na (0.3 wt%)	Si (46 wt%), Al (1.6 wt%), and Na (0.5 wt%)	Si (44.9 wt%), Al (1.3 wt%), and Na (0.7 wt%)

“Normal” (~3% H2O) Saturated Air Conditions



Figure 2 – Fibres post-exposure for “normal” conditions: quartz wool (left), insulation 1 (middle), and insulation 2 (right).

Table II. Comparison of appearance and Cr(VI) content for “normal” conditions.

	QUARTZ WOOL	INSULATION #1	INSULATION #2
Color	Light green, light yellow, light brown	Light green to light brown	Light brown
DPC Results	0.8 – 1.0 ppm	0.1 – 0.2 ppm	0 – 0.1 ppm
ICP-MS Results	224 mg/kg	139 mg/kg	96 mg/kg