

Organochlorine compounds in aluminium degassing with hexachloroethane

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1. Introduction

Hydrogen gas from ambient water vapour is easily dissolved in molten aluminium causing porosities and impaired mechanical properties in the solid state metal. Degassing is therefore often necessary, particularly in aluminium foundries^{1,2}. Hexachloroethane (HCE) has been used as a degassing agent in secondary aluminium smelting since the late 1930's³. Although previously considered fairly benign, recent studies of the emissions from HCE based aluminium degassing^{4,5} have shown an unexpectedly high yield of some more complex organochlorine compounds (OCC), particularly hexachlorobenzene (HCB), a porphyrinogenic and a carcinogenic substance⁶. For reasons of environmental protection there is an international tendency to restrict HCE consumption^{7,8}. The present worldwide annual HCE market, however, is still about 3 500 tonnes⁹ out of which the bulk probably is used for aluminium degassing. The purpose of the present study was to determine qualitatively and quantitatively a wider spectrum of substances formed during HCE based degassing with special reference to the emission of OCC.

2. Material and methods

The degassing was carried out in a foundry designed for education and research. The experimental set-up consisted of an electrically heated furnace equipped with an exhaust hood and a frontal opening permitting access to the melt. The furnace was charged with 70 kg of an aluminium alloy (SS-4261; 88% Al, 12% Si) and after melting the temperature was held at 740°C during the entire experiment. For degassing 0.12% (w/w) HCE (Degaser 200, Fosco AB, Sweden) was introduced to the melt by lowering the chemical to the bottom of the melt through the hood opening. To accomplish detectable levels of chlorinated dioxins (PCDD) and dibenzofurans (PCDF) this procedure had to be repeated in 20 minute cycles (n=30) which included alternate artificial regassing with sodium tetrahydroborate (Dycastal, Fosco AB, Sweden). The gas level was checked periodically and found to be stable and realistic. In a final series of degassings the amount of HCE was progressively increased.

Chlorobenzenes, chlorophenols, PCDD, PCDF and polycyclic aromatic hydrocarbons (PAH) were sampled in the exhaust duct according to standard procedures. Particle, condensed liquid, and gas samples of the exhaust fumes were collected using a glass probe, a filter, a cooler, a glass flask for the condensed fraction and an XAD-2 column for

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the gases and vapours^{9,10}. Analysis was performed with high resolution gas chromatography and mass spectrometry¹¹.

HCE and octachlorostyrene (OCS) were sampled with filter monitors and analysed as above. However, the sampling of these substances was obtained under non-isochinetic conditions, and the emission data had to be adjusted. Hydrochloric acid (HCl) was sampled with an impinger bottle and analysed with ion chromatography. Carbon monoxide (CO) as well as total hydrocarbons (THC) were measured with direct reading instruments.

3. Results

The emission of various compounds in the exhaust fumes is expressed in relation to the HCE added to the melt. By far, HCl and THC dominated in the smoke followed by CO (Table 1). The quantum yield of OCC was highest for the chlorobenzenes, particularly HCB (5.5 mg/g HCE), for OCS (0.9 mg/g HCE), and unreacted HCE. The emission of these substances was 10^4 - 10^5 times higher than for the PCDD and PCDF, which were equally dominated by the highly chlorinated congeners (hexa-, hepta-, octasubstituted). The formation of chlorophenols was intermediate, mainly consisting of pentachlorophenol (92%). The emission of PAH, dominated by benzo(a)pyrene (63%) and naphthalene (33%), was low.

With increasing levels of HCE added to the aluminium melt, the ensuing change in emission varied between substances. Among the OCC, the most prominent increase was observed for unreacted HCE (Figure 1).

4. Discussion

With the recommended HCE additive to the molten aluminium there was a good agreement in this experiment with previous findings⁹ as to the quantum yield of HCB. Variations between the studies in temperature, type of aluminium alloy used and other factors does not seem to have been of major importance. The data for OCS, an environmental pollutant with a toxicological profile similar to HCB¹², and unreacted HCE (Table 1) are not exact but they should be within the correct order of magnitude indicating that aluminium degassing may be a significant source of OCS. The formation of PCDD and PCDF was much lower but given the worldwide HCE consumption for aluminium degassing over the decades, the total contribution of PCDD/PCDF from this source might still be of interest. Since technologically and commercially equivalent but less toxic methods for aluminium degassing are available, further use of HCE does not seem to be justified.

5. Conclusions

A high quantum yield of biologically stable OCC, particularly HCB and OCS, was found in aluminium degassing with HCE. The findings are in good agreement with previous studies, and this degassing technique should be discontinued.

Table I. Exhaust fume emissions in HCE based aluminium degassing

Substance	mg/g HCE
Σ PCDD	$4.0 \cdot 10^{-6}$
Σ PCDF	$4.7 \cdot 10^{-4}$
Σ Chlorobenzenes	5.9
Hexachlorobenzene	5.5
Σ Chlorophenols	$5.2 \cdot 10^{-2}$
Σ Polycyclic aromatic hydrocarbons	$7.0 \cdot 10^{-4}$
Hexachloroethane	0.6
Octachlorostyrene	0.9
Hydrochloric acid	400
Total hydrocarbons	261
Carbon monoxide	28

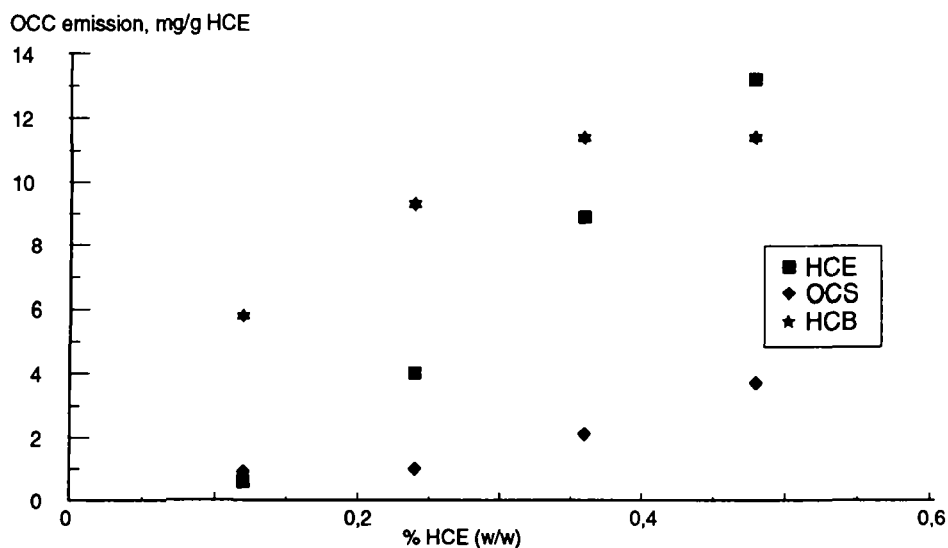


Figure 1. Emission of some OCCs with increasing HCE additive in aluminium degassing.

6. References

- 1) Boddey RF. The use of chemicals in the modern foundry. *Ann Occup Hyg* 1967;10:231-239.
- 2) Kanicki DP, Rasmussen WM. Processing molten aluminium - part 2. Cleaning up your metal. *Modern Casting* 1990;80:55-58.
- 3) Bunbury FM. Foundry Services Limited - 50 years of successful innovation. *Foundry Trade Journal* 1982;153:75-111.
- 4) Maier K. Die Entstehung von Hexachlorbenzol bei der Schmelzebehandlung von Aluminiumlegierungen. *Giesserei* 1988;75:149-152.
- 5) Månsson L, Seldén A. Emission of organochlorine compounds from an aluminium remelting plant. 1st jornadas nacionales sobre hexaclorobenceno, Barcelona, 1988. Barcelona, Publicaciones del Seminario Pere Mata de la Universidad de Barcelona. 1990;41:73-75.
- 6) Morris CR, Cabral JRP. Executive summary. In: Morris CR, Cabral JRP, eds. Hexachlorobenzene: proceedings of an international symposium, Lyon, 1985. Lyon, International Agency for Research on Cancer 1986:XIII-XVIII (IARC Sci Publ No 77.).
- 7) Anon. List of measures. Part (a) agreed measures. Annex 1B to the Ministerial Declaration, Third International Conference on the Protection of the North Sea. The Hague 1990, p. 22.
- 8) Anon. Oslo/Paris Commission bans hexachloroethane. *European Chemical News* 1993, July 5, p. 26.
- 9) Hellén G. Dust measurements in emissions to air from permanent facilities. Swedish Environmental Protection Agency, PM 1821. Stockholm 1984, 49 pp. (in Swedish).
- 10) Jansson B, Bergvall G. Recommended methodology for measurement of PCDD and PCDF in the Nordic countries. *Waste Management and Research* 1987;5:251-255.
- 11) Warman C. A method for sample preparation and analysis of organic compounds in gases and ashes. Environmental Consultants, Technical report 64. Studsvik 1989, 9 pp. (in Swedish).
- 12) Smith AG, Carthew P, Francis JE, Ingebrigtsen K. Influence of iron on the induction of hepatic tumours and porphyria by octachlorostyrene in C57BL/10ScSn mice. *Cancer Lett* 1994;81:145-150.