Removal of Toxic Chlorine-Containing Chemicals by Zirconium Hydroxide-Based Sorbent Media

Joseph A. Rossin and Gregory W. Peterson

Guild Associates, Inc., Dublin, Ohio USA

Background: Current respirator filters for toxic chemical removal typically utilize impregnated, activated carbons. Carbon-based adsorbents designed for the removal of toxic vapors are comprised of a porous substrate onto which metal impregnants are dispersed. The pore structure is responsible for removing vapor phase contaminants via physical adsorption, while the impregnants provide a route for the removal of vapor phase contaminants via chemical reaction. Although carbon-based materials are effective in removing a wide range of toxic chemicals from streams of air, the material is not without its drawbacks. First, the capacity for the removal of high volatility gases is low, being limited by the impregnant loading of approximately 10% metals by weight. Higher metal loadings result in a decreased metal dispersion, which leads to the physical blocking of pores and an overall reduced effectiveness. Second, the metal impregnants are not well dispersed leading to poor utilization of the metals. Third, the metal impregnants have a tendency to migrate to the external surface of the carbon granule as a result of prolonged environmental exposure, leading to decreased filtration performance. Zirconium hydroxide, $Zr(OH)_4$, has recently been identified as a reactive substrate capable of removing a wide range of reactive gases that include sulfur dioxide, hydrogen cyanide and cyanogen chloride. The high density of hydroxyl groups allows for a large capacity against acidic gases. The high capacity is attributed to the substrate contributing to the reaction chemistry. In this study, we report the ability of $Zr(OH)_4$ based media for the removal of chlorine-containing toxic chemicals, examples of which include chlorine, phosgene, and hydrogen chloride.

Methods and Approach: Cl_2, $COCl_2$ and HCl breakthrough curves were recorded using $Zr(OH)_4$, $Zr(OH)_4$ loaded with TEDA, and $Zr(OH)_4$ loaded with zinc plus TEDA. All media were tested as 20 x 40 mesh granules. Media was characterized for surface properties prior to and following exposure using XPS. N_2 adsorption isotherms were recorded to assess porosity.

Results and Discussion: Zirconium hydroxide provided only minimal capacity for the removal of Cl_2 and $COCl_2$. The addition of TEDA to the formulation greatly enhanced the ability of the material to remove these vapors. This enhancement was attributed to TEDA promoting the hydrolysis of Cl_2 and $COCl_2$. The addition of zinc to the formulation further enhanced the filtration capability of all vapors investigated. Breakthrough times exceeding those associated with activated, impregnated carbon were achieved. For example, the zirconium-based media achieved Cl_2, $COCl_2$ and HCl breakthrough times of 53, 45 and 150 minutes, compared with times of 38, 25 and 60 minutes for carbon-based media.

XPS analysis revealed the presence of surface zinc and zirconium chloride species. There was also evidence that chlorine interacted with TEDA. The surface of the zirconium-based media consisted of both terminal and bridging hydroxyl groups. Only the terminal hydroxyl groups were able to contribute to the removal of the chlorine gases.

Preliminary Conclusions: $Zr(OH)_4$ based media is effective in the removal of chlorine-containing vapors. The addition of TEDA to the formulation is necessary to facilitate hydrolysis reactions.