KEYNOTE SPEAKER

THE ROLE OF CHLORINE IN HAZARDOUS WASTE INCINERATION

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Industrial incineration with energy recovery using hazardous, industrial and municipal waste as fuel plays an important role in decomposing toxic organic substances, as well as immobilizing toxic elements from heterogeneous, complex waste streams in order to minimize leakage into the environment and ecosystems, which may occur in case of landfilling. Even though the net effect of incineration on the environment is positive compared to landfilling, it is of great importance to minimize any adverse effects on the environment. It turns out that chlorine plays a key role in many of these processes:

- Volatilization of metals
- Oxidation of metallic mercury to water soluble Hg(II)
- Formation of chloride rich deposits on the boiler tubes causing high temperature corrosion and dioxin formation
- Enhancing the sulfur capture capability of lime
- Causing corrosion in the wet flue gas treatment equipment
- Emission of chloride salts to the recipient and HCl + Cl_2 to the atmosphere
- Influencing the leachability from ashes

A key to understanding the fate and influence of chlorine in industrial incineration processes is the material transfer coefficients of both chlorine and how it affects other elements. The chloride salts of many metals are more volatile than their corresponding oxides, hydroxides, sulfates or carbonates. In particular, sodium, potassium, zinc and lead form volatile chloride salts which may nucleate to aerosols to and condense on small particles and on the boiler tubes where they form sticky deposits and increase high temperature corrosion. As a consequence of the chlorine aided volatilization of the mentioned substances, a high concentration of these substances are found in the fly ash. This gives the opportunity to extract for example alkali metals, lead and zinc from the fly ash using acid leaching with the 3R or ReZinc process, using HCl from an acidic wet scrubber.

A high chloride content in the boiler tube deposits in the temperature window 200-450°C leads to formation of dioxins and furans. This formation of dioxins and furans can be suppressed by decreasing the chloride concentration in the boiler deposits by adding sulfur to the fuel, which promotes sulfation of the dioxin forming chloride salts to inert sulfate salts. Alternatively, sulfur can be recirculated back to the boiler from the flue gas cleaning using the Sulfur Recirculation process, which has been demonstrated to decrease the high temperature corrosion in the superheaters significantly as well as the dioxin formation and dioxin emissions by 70% in full-scale operation.

In the gas phase, chlorine exists mainly in two different forms: hydrochloric acid (HCl) and chlorine gas (Cl_2) in equilibrium with each other described by the Deacon equilibrium. Even though the dominating species is HCl, trace amounts of the powerful oxidant Cl_2 plays an important role in oxidation of of metallic mercury to water soluble Hg(II) which in turn has higher removal efficiency in both dry and wet flue gas cleaning systems. The MercOx process may be applied where the chlorine available in the fuel is not enough to oxidise the metallic mercury sufficiently.

In dry lime based flue gas treatment systems, removal of HCl leads to formation of Ca(OH)Cl, which plays a key role in decreasing the stoichiometry for removing SO_2. In wet scrubbers, HCl may be removed in an acidic stage by just adding water due to its high solubility. However, Cl_2 is only sparingly soluble in water and may be removed by reducing it to chloride with the aid of a reducing agent. The corrosive properties of HCl and chloride salts, limits the materials of construction that can be used in a wet flue gas cleaning system. Normally the main parts are manufactured in FRP (Fiber reinforced plastics) and PP (Polypropylene), but since these have poor thermal conductivity, heat exchangers and temperature measurement devices are usually manufactured in expensive, corrosion resistant metallic materials.

The requirements for chlorine removal efficiencies are expected to increase in the future with the introduction of even more stringent emission limits as well as the introduction of post combustion carbon capture technologies, where chlorine may lead increase corrosion and solvent degradation.

In summary, chlorine plays a key role in the formation and removal of various pollutants, influencing environmental performance as well as high and low temperature corrosion, impacting construction, operability and maintenance requirements for industrial incinerators.