PVC and waste incineration - modern technologies solve old problems

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Abstract

Waste incineration is more and more a necessity, in order to tackle the rapidly rising amounts of Municipal Solid Waste (MSW) generated in China's large Cities. Similarly as in Europe and the U.S.A. the Nimby (Not in my backyard) syndrome holds strong in China. This irrational attitude is strongly stimulated by fear from dioxins. Following the example from the E.U. China could build additional trust in MSW incineration, based on strict emission standards supported and enforced by stringent controls. Dioxin generation has been associated with incineration ('dioxin factories') and at times also with PVC. In this paper the problem is analysed rationally and the various factors are put into their proper perspective. In a second paper aspects of MSW incineration and associated flue gas cleaning are highlighted.

1. Introduction

After 150 years of continuous steady development and evolution **Municipal Solid Waste incineration** (MSWI) is still a topical subject today, if not in Europe [1], then for sure in China. Currently, China has a pressing need for more incinerator plant, to reduce its mountains of MSW [2]. In the past 30 years **PVC** likewise has been at the centre of fierce debate. Together, waste incineration and PVC were held responsible for scores of problems, ranging from the emission of dioxins to the wastage of superheater tubes. In this paper, PVC is briefly introduced and these issues are revisited. Some major facts regarding various impacts on incineration and dioxins are presented in a synthetic yet systematic manner.

The presence of plastics at large has serious consequences on the heat balance and capacity of incinerator plants. In addition, it is important that these plastics are well mixed into the feed of Municipal Solid Waste (MSW). PVC is somewhat particular, since its heating value is closer to that of wood than to that of oil or polyolefins. Its thermal behaviour and that of its additives is briefly analysed in this incineration context.

During incineration, waste PVC acts as a source of both heat and gaseous hydrochloric acid (HCl). Under ideal circumstances, these can be recovered and put to good use. Potential impacts, however, are the volatilisation of heavy metals and alkali (mainly derived from vegetal and wood waste) as chlorides and interference in complex corrosion mechanisms that under adverse circumstances will markedly reduce the lifetime of superheater tubes in high-pressure steam boilers. The presence of PVC may also influence the amount and composition of flue gas cleaning residues and affect their subsequent treatment. These various phenomena are briefly analyzed, with reference to some major studies (whether produced by scientific sources, by industry, or its opponents) as well as to personal experience in areas of dioxin studies and of troubleshooting incinerator plants. The European PVC industry has also been conscious about these different problems, potentially affecting the image of its products. Showing responsible and pro-active behaviour, now 10 years ago, it founded VINYL 2010 with the purpose of realising a number of ambitious goals, destined to diminish the PVC-footprint. Some of these initiatives, i.e. those relevant to waste management, are briefly highlighted.

2. Polyvinylchloride (PVC): portrait and products

PVC is a most versatile plastic, combining low cost and durability, versatile appearance and dependable performance with ease of processing. After polyethylene and polypropylene it is the third largest-selling commodity plastic in the world and the material of choice for healthcare, IT, transport, textiles, and construction. PVC is essential to the construction industry, given its resistance to light, chemicals and corrosion. It is applied as profiles, ducts, gutters, cable sheathing, flooring, roofing, or washable wallpaper. It also appears in numerous leisure and safety features and in furniture, art & design. As a water resistant coating for fabrics it protects merchandise, as well as personnel from rain.

PVC is derived from salt and oil. The electrolysis of brine jointly produces sodium hydroxide, hydrogen and chlorine:

$$2NaCl + 2H_2O + \text{energy} = 2NaOH + Cl_2 + H_2$$

Sodium hydroxide is a major caustic chemical and chlorine is essential in numerous chemical and pharmaceutical syntheses, whereby it is converted into HCl. 'Oxychlorination' of HCl regenerates chlorine that combines with ethylene[2] obtained from oil, forming ethylene dichloride and eventually vinyl chloride monomer (VCM). Molecules of VCM are then polymerised to form PVC resin, to which appropriate additives are incorporated to make a customised PVC compound. As a base resin, PVC is oil-thrifty and its composition can best be visualised as 43% of oil and 57% of brine.

Rigid PVC (or PVC-U, for un-plasticised) is thermally unstable at the temperature range of melting and formgiving (conversion). Thus, it is compounded with heat stabilisers and lubricants. Stabilisers bring metals, such as lead, organotin, barium/zinc or calcium/zinc in the formula. **Flexible PVC** is softened, made resilient and easier to handle by

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[2] In China, the traditional route over carbide acetylene (produced from coal and limestone) is more widespread.

addition of **plasticisers.** Other frequently used **additives** are processing aids, impact modifiers, thermal modifiers, UV stabilisers, flame retardants, mineral fillers, pigments, or even biocides, blowing agents… for specific requirements.

3. Municipal Solid Waste incineration [1]

Public cleansing and collection and treatment of waste are essential for urban hygiene: putrescence generates foul odours and Municipal Solid Waste is obnoxious, due to the presence of germs and pathogens, eggs of parasites, viruses, and of pollutants, such as heavy metals, toxic organics, etc. It is also a source of fires. Landfilling waste may lead to long-lived landfill fires; migrating leachate pollutes aquifers; infiltrating landfill gas has caused deadly explosions. Almost all these hazardous properties are eliminated and destroyed by incineration. Moreover, incineration reduces volume by a factor of 10 to 20 and leaves a sterile residue. In numerous E.U. countries bottom ash is treated and reused as a low grade civil works material, further reducing residues from incineration by putting these to good use.

Municipal Solid Waste (MSW) is variable and unpredictable in its composition and properties. Tanner, an early Von Roll collaborator, devised a triangle diagram for representing refuse composition, expressed as a ternary mixture of Moisture, Ash, and Combustibles. These simple concepts are of paramount importance in the design and operation of a **Combustion Chamber.** Indeed, more moisture prolongs the drying time before waste will ignite. Once dry waste heats up rapidly while receiving radiant heat from furnace walls and roof of the combustion chamber. Ignition proceeds when the combustible fraction C thermally decomposes, emitting its **Volatile Matter** under the form of flammable vapours and gases. The latter ignite, resulting in fast, flaming combustion, proceeding at the pace of their thermal decomposition. Fast combustion, however, locally depletes oxygen creating reducing gas volumes containing carbon monoxide and non-combusted volatiles. Hence, all depends on macro and micro-mixing conditions, whether such puffs are either fully combusted or emitted as a CO and TOC-peak. **Fixed Carbon** takes longer to be consumed by fire, either because of size (a block of wood, a telephone book), or of occlusion in ashes limiting air access. From this discussion it follows that both moisture content and Fixed Carbon burnout determine the residence times required on a grate, whereas flaming combustion demands sufficient furnace volume for flames to develop and burn out. In a Tanner diagram China's refuse is situated outside the domain of sustained combustion: auxiliary fuel must be on hand!

3.1. Thermal and weight capacity – Higher Heating Value

Mechanical grates. Incinerator furnaces are characterised by a minimum and a maximum **thermal capacity (MW)**. Below a minimum value the heat generation rate is so low that the furnace no longer reaches adequate temperatures to ensure smooth drying, heating and ignition, and eventually complete combustion. When the flue gas temperatures descend below 850°C, European Codes stipulate that **auxiliary burners** must ignite and heat the gases, to ensure a sufficient burnout. Excessive combustion temperatures are also undesirable, because fly ash becomes too tacky, creating deposits on furnace walls and boiler tubes. Ash similarly starts slagging; the resulting deposits on the furnace walls become ampler and ampler, eventually even restricting the movement of waste on a grate.

Furnaces feature also a **weight capacity** (Mg/h), dictated by the necessity to maintain coverage of the grate: some strict minimum for protecting grates against furnace radiation and atmosphere and a maximum related to bed density. Finally, the relation between thermal and weight capacity is also bounded, by the necessity of producing sufficient hear for heating furnace and waste; the ratio represents the heat of combustion (MJ/kg). These different boundary conditions are represented in thermal capacity vs. weight capacity diagrams, indicating the area of smooth operation of the plant. The latter is extended towards low Heating Values by preheating combustion air, or towards high calorific waste by cooling the combustion chamber. Thus, there are links between furnace requirements and waste characteristics.

Fluid bed furnaces provide fast combustion already at low temperature (600-850°C). In **bubbling fluid bed** most combustion takes place in the freeboard zone located above the bed; the latter should be ample and well mixed, so that reducing and oxidising strands can mix and burn out completely. Secondary air provides the required swirl for mixing. The fluid bed provides a thermal flywheel that effectively copes with short-term fluctuations. In China **circulating fluid bed** units are unusually popular, since combustion stability can be maintained simply by adding cheap coal, stead of using expensive oil.

Incinerators are thermal units: liberating more combustion heat also requires supplemental combustion air: a simple rule of thumb states that this amount is directly proportional to the Higher Heating Value, whatever the fuel (gas, oil, garbage). A generic problem with plastics is that their air requirements are so high; PVC, however, comes closer to wood:

Table 1. Some Higher Heating Values

Fuel	Wood (15% moisture)	PVC Resin	Anthracite (4% moisture)	Gas oil
Higher Heating Value, MJ/kg	16	26	36	46

3.2. Thermal decomposition

Organic materials decompose upon heating, generating generally smaller and simpler molecules. The emerging volatiles contain inorganic (CO, CO_2, H_2O, H_2…) as well as aliphatic and aromatic organic compounds; their product distribution depends on numerous factors, such as temperature, raw materials, residence time of volatiles and solid fraction, and catalytic effects exerted by ash, bed material or furnace walls. Primary products show structures close to those of the molecules pyrolysed. The longer the residence times, the more the structures evolve towards more thermally stable molecules. Ultimately, in the absence of air mainly carbon, hydrogen, and water vapour remain. Vinyl compounds (polyvinylchloride, -hydroxide, -acetate) decompose at unusually low temperatures. PVC decomposes even in two steps. The first step boils down to:

$$CH_2{=}CHCl = {-CH{=}CH{-}} + HCl$$

In PVC decomposition HCl evolves almost quantitatively between 225 and 275°C. This first step also produces some benzene. The rate of dehydrochlorination depends on the stabilizer package used, molecular weight, the presence of oxygen and hydrogen chloride, and crystallinity. The second step yields further, mainly aromatic compounds, by internal cyclisation [3].

Polyolefins pyrolyse at higher temperature, attaining a maximum rate of decomposition at ca. 450°C [4]. Primary products are polyolefinic and paraffinic chain fragments following a Gaussian Molecular Weight distribution: the higher the temperature, the shorter the resulting product molecules. Secondary products from polyethylene, as well as primary products from polypropylene show more branched chain products.

Most waste in China is organic and either cellulose or protein based, even though the share of plastics is in progress, in particular in Large Cities.

Several researchers have studied the pyrolysis and combustion of PVC. Both have also been scrutinised from a view of dioxin formation. The fingerprints produced are definitely distinct from the *thermal fingerprint*, typical in MSWI. Obviously, there is no *specific* role for PVC in dioxin formation, since it decomposes even earlier than most other plastics, although any organics or HCl emanating from it could contribute to dioxin synthesis, same way as wood, cellulose, lignin, or other plastics could.

3.3. Chlorides and chlorine in pyrolysis and combustion

Most wastes contain chlorides and also chlorinated organic compounds. The Bundesweite Hausmüllanalyse (comprehensive analysis of refuse and its sorting fractions in the German Federal Republic) established the amount of, e.g., heavy metals, PAH, and dioxins in MSW for fractions such as fines, vegetal, synthetic, paper & board. All of these are contaminated with all kinds of pollutants [5]. During incineration these organics are destroyed and the chlorine converted to HCl. Typically 50 % of the Cl-content comes from PVC [1].

This share of PVC gains in importance, in case PVC is widely used in packaging; this was the case in France during the nineties, because of mineral water bottles (now in PET). There was no indication that French incinerators generated more dioxins because of such a larger share of PVC.

During combustion PVC, NaCl as well as a vast majority of organic and inorganic chlorinated compounds are converted into HCl. PVC liberates HCl very easily. Such release is also likely to be complete, unless some other compounds, e.g. $CaCO_3$, captures it; the latter is plausible in numerous applications featuring fillers of precipitated calcium carbonate or ground dolomite/calcite. At high temperature NaCl reacts with steam, yet its conversion into NaOH and HCl is limited by thermodynamic equilibrium; it shifts largely to the right, however, in case NaOH is itself converted into silicates, aluminates, or other composite compounds [6].

3.4. Formation of Chlorine – Thermodynamics and kinetics

Thermodynamically, the formation of chlorine gas from hydrogen chloride is described by the Deacon equilibrium:

$$4\,HCl + O_2 = 2\,Cl_2 + 2\,H_2O + \text{Heat}$$

At combustion temperatures, HCl is by far the main Cl-compound yet – below 500°C – equilibrium conditions reverse and elemental chlorine gains ground. Fortunately, this reaction also becomes slower and slower, so that equilibrium is frozen during the few seconds separating flue gas from furnace to stack. The Deacon reaction also shows an effect of oxygen partial pressure, an even stronger effect of water vapour, as well as an effect of total pressure. The other halogens follow similar equilibriums, with the elementary amount rising in a sequence: $F_2 < Cl_2 < Br_2 < I_2$. The Deacon reaction is a potential source of both corrosion and dioxin. No doubt, chlorine is only rarely produced in significant quantities". This requires the presence of oxidants, such as iron ore (Fe_2O_3) or manganese ore MnO_2.

3.5. Additives

Prior to its multiple uses PVC is compounded with various additives, so that its properties are tailor-made to each particular application. Flexible vinyl contains plasticisers; these are almost entirely converted during combustion: only traces can still be identified in incinerator flue gas. Through stabilizers and pigments PVC also contributed to the Cd-load (in some products produced until 2001) and to the Pb-load (lead will be phased out latest by 2015 in the E.U.) of MSW. The aforementioned Bundesweite Hausmüllanalyse thus contributed to render MSW cleaner, i.e. leaner in heavy metals, by banning their use. In 1983 MSW still contained 10-15 ppm Cd [5]. Heavy metals, such as Cd, Pb, Zn, during incineration mainly report to the fine fraction of fly ash.

3.6. Conclusions

Incinerators are thermal units, in need of calories to sustain the process, yet also limited in capacity by the same calories. In China the problem at present is sustaining combustion, rather than excess heat. Each entering element brings along certain consequences and is subject to partition, yet it is unfeasible sorting out entirely any of all elements represented. PVC brings an input of calories, as well as of chlorine, yet its chlorine contribution is not an issue, since any obnoxious element entering the incinerator will be controlled appropriately by flue gas cleaning.

4. Dioxins and Incineration

More than a century ago dioxins first drew the attention, while their synthesis affected laboratory workers with chloracne. The same happened after isolated incidents in chemical industry, e.g. Monsanto at Nitro, BASF at Ludwigshafen, or Philips-Duphar at Amsterdam. A more spectacular accident occurred at Seveso (N. of Milan): after a runaway in a herbicide reactor its contents were vented all over Seveso, causing trees to loose their leaves, death to various animals, as well as the evacuation of 10,000 inhabitants (1976). People then exposed to dioxins are still being monitored today, to detect any eventual symptoms or mortality. Epidemiological investigations show the appearance of rare, soft-tissue cancers and neurological afflictions, yet no net increase in mortality.

Only one year later dioxins were discovered on fly ash from the (old) Amsterdam incinerator. Soon, there was major conjecture about the origins of these unwelcome compounds and various mechanisms were proposed to explain their possible origins. Scientists from Dow Chemicals argued that dioxin formation is related to 'Trace Chemistries of Fire'. Chemical synthesis from related compounds (polychlorinated phenols, biphenyls, benzenes…) formed the basis of various 'precursor' theories. In 1985 Vogg and Stieglitz launched 'de novo' theory, involving low temperature catalytic oxidation of 'carbon', also generating a wide array of Products of Incomplete Combustion. Those include polychlorinated benzenes, phenols, naphthalenes, biphenyls, and – of course – dibenzo-p-dioxins and dibenzofurans. Stieglitz methodically investigated the different steps of 'de novo' formation from 'carbon', i.e. catalytic chlorination, oxidative catalytic breakdown of chlorinated structures, and regeneration of the reduced catalyst by oxidation. Transition metals are most mentioned and copper chloride and oxide have proven to be an outstanding catalyst. Also iron chlorides/oxides may be active. Although a number of substances have been tested and proven to be active the precise nature of dioxin forming catalysts is still unknown. High temperature volatilisation of chlorides, followed by low temperature de-sublimation is another route suggested.

4.1. PVC and dioxins

Should dioxins enter together with PVC and other plastics (both readily absorb any gaseous dioxins, present in the air) then the fire will destroy these dioxins nearly completely. Dioxin levels leaving the furnace are almost undetectable at high temperature and much less than the amount of dioxins present in either raw MSW or flue gas, generally 3-10 ng TEQ/Nm^3 (new plant) or 10-100 ng TEQ/Nm^3 (obsolete plant). The dioxins in raw flue gas are newly formed during the cooling of flue gas in the boiler or its cleaning in an Electrostatic Precipitator. The latter operates like a real dioxins factory at operating temperatures exceeding say 240°C. Indeed, until recent years MSW incinerators formed a large source of dioxin emissions, yet at the same time they eliminated those dioxins entering with MSW, cf. [5,7].

Several pathways each may explain dioxins formation. One important factor is the formation of Products of Incomplete Combustion (PICs), always present (typical TOC < 5 mg/Nm^3) in the flue gas, whether as miscellaneous organics, hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAHs), or 'soot'. Each may lead directly or indirectly to the structures present in 'dioxins', more precisely polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF). Three theories compete, namely the precursor theory, in which dioxins form from structurally related compounds such as chlorophenols, the 'de novo' theory in which soot is catalytically chlorinated and then partially oxidised, creating 'new' dioxin structures, and a third theory, in which the basic structures pre-exist already at more elevated temperatures and are chlorinated at lower temperatures.

PVC may give rise to dioxins, exactly as paper, plastics, garden waste, and other MSW components might. There is no particular reason why one source of the elements C, H, O, and Cl, would be markedly more proficient than another. Dioxins are associated with the evolution of Products of Incomplete Combustion (PICs). During combustion these are permanently formed at some rather low level (few mg/Nm^3), yet strongly amplified during each combustion set-up and accompanied by brief pulses of carbon monoxide CO and Total Organic Carbon (TOC). To avoid these peaks it is necessary to mix MSW thoroughly and avoid large amounts of high HHV-waste that take fire simultaneously. The problem was analysed in a case study involving a fluid bed unit with periodic overfeeding [8].

4.2. Salient factors in dioxins formation

Significant factors affecting dioxins formation are quite large in number, yet to be subdivided into two groups; a first related to **operational factors**, a second to **chemical and catalytic factors**, such as: catalysis, carbon, oxygen, water vapour, and chlorine. Each of these has several impacts, with various mutual interactions and it is unlikely that their ranking and relative importance under varied conditions in diverse systems will ever be established once and for all.

Operating factors are of paramount importance. **Poor combustion conditions** result from 'bad' waste, i.e. either too poor or too rich, and appear as a consequence of locally insufficient oxygen and mixing of oxygen-rich and oxygen-lean combustion products, or inadequate **t**emperature, residence **t**ime, and **t**urbulence (3 T's). These 'bad' operating conditions not only lead to more PICs and PAHs (a small fraction of which converted into dioxins), but also to a prolonged increase in dioxins (memory effects: PICs adsorb on boiler deposits and still continue generating dioxins a day after). Poor combustion conditions result often from feeding too much at a time, without adequate pre-mixing wastes of different origins and quality. Combustion upsets are notable by a development of peaks of carbon monoxide accompanied by Total Organic Carbon (TOC), a measure for the amount of PICs present. Combustion conditions may be improved by both technology (grates, furnace geometry) and operating skills (mixing and feeding waste, providing primary and secondary air). Nevertheless, firing fuels such as MSW always bring in a factor of chance. With respect to dioxins the following factors may help:

- Well-mixed, homogeneous waste. Humidity transfer and dispersion of high calorific waste (plastics & rubber) in MSW are positive factors, i.e. prolonged storage and periodic mixing of the bunker's content.
- Low rates of primary air. This reduces the entrainment of dust particles, a source of dust deposits and boiler fouling and corrosion, as well as the amount of oxygen excess in the flue gas.
- Homogeneous combustion. No large packs of high calorific waste taking fire together.
- High quality mixing of gases exiting the furnace.
- Ample post-combustion volumes at adequately high temperatures.
- Designing post-combustion volumes by means of Computer Fluid Dynamics for good mixing, avoiding short-circuiting as well as dead zones.
- Avoiding building deposits on boiler tubes, collection plates in E.P.'s, in flues, etc.
- Operating E.P.'s at low temperature, by extending waste heat boiler surfaces and limiting boiler fouling.

The quality of operation can be judged by the occurrence of **CO-** and **TOC-peaks**. Ideally, their frequency should be nil, on a daily basis. Should such peaks still occur, they can be termed serious (CO = 10^3-10^4 mg/Nm3), medium (10^2-10^3 mg/Nm3), or benign (10-10^2 mg/Nm3). TOC-peaks concur with CO-peaks, yet their height and width differ. The reason for such short-lived peaks is either overfeeding (too much at a time) of fluid beds, or inadequate mixing.

Although complete combustion, mixing by blowing in secondary air at high speed and absence of set-ups are all primordial operating factors, definitely less dioxin is formed in case excess oxygen is limited.

Another important operational area is related to the cooling of flue gas: fast and deep cooling limits the formation of dioxins. Slow cooling in contact with deposit dust has an opposite effect. For small plants, e.g. metal foundries, quenching off-gas is suitable a prevention measure.

Dust removal also takes dioxins away, especially at low temperatures. Baghouse filters are designed to clean gas down to the very low dust levels required to reach the level of 0.1 ng TE/Nm^3. Any imperfections should be observed by means of tribo-electric sensors, opacity measurement, etc.

Chemical and catalytic factors. Probably the most important chemical factor is the presence of **transition metals** providing the required catalytic influences: the latter not only must fix chlorine on carbon structures, but also oxidise the latter, so that dioxins (together with scores of other surrogate and precursor compounds) are liberated. Catalytic metals are likely to be finely divided and associated with **particulate**, in particular its finest fraction. The latter receives desublimating metal salts (Zn, Pb, Cu, Cd…), after having been volatilised at flame temperature, or even lower, as is the case for chlorides. Obviously, **copper** is a premium catalyst. Depending on the source, dioxins are formed according to the second order, or rather less so, of copper concentration. Copper is often better represented in fly ash from fluidised bed units than in that from mechanical grate units. This could be due to erosion effects, enhancing copper. In China, fly ash is much leaner in heavy metals than in the E.U. Another catalytic metal is always well represented: iron oxides. Mixing fly ash with inert materials and carbon creates de novo, dioxin-generating activity.

Thus, particulate is important. So is the supply of **oxygen** to the system: after chlorinating carbon or oxidising carbon-structures, the catalyst is in its reduced form. Oxygen restores a higher valence, required for reactivity. A next factor is **carbon.** This is also a black horse, since the relations between carbon structure and dioxin formation are all but elucidated. Finally, there is **chlorine.** The presence of chlorine is essential in dioxin formation. On the other hand, chlorine is one of the most ubiquitous elements and the question always arises where chlorine comes from? In really chlorine lean systems (e.g. copper cathodes + natural gas) dioxins still form even though the sources of chlorine remain obscure and difficult to trace. Greenpeace contends that PVC is salient. This is manifestly untrue in any incineration system, for chloride is plentiful and any pathway starting at the structure of PVC and ending at those of PCDD and/or PCDF would be long and tortuous and crossing a multitude of other pathways. Factors of influence are so numerous and their effects are manifestly so complex that any direct links with PVC can be excluded!

5. Flue Gas Cleaning

In MSWI flue gas cleaning is essential. Public and political pressure have been so powerful that at present MSWI is the most regulated and best controlled form of combustion. Flue gas cleaning addresses successively:

- Particulates and dust, including associated heavy metals.
- Acid gases, such as HCl, HF, and SO_2.
- Nitrogen oxides NO, NO_2, and N_2O.
- Semi-volatile organic compounds, such as PAHs, PCDD/Fs (dioxins) and PCBs.

HCl is an acid, irritating gas, yet it is eminently soluble in water and thus easily scrubbed out from flue gas (together with HF and HBr, both present at about 100 times lower concentration levels). The resulting diluted solution can be distilled to yield a commercial concentration. An alternative is using it as a leaching agent, to remove heavy metals from fly ash. In case such recovery options are not followed yet, the acid needs to be neutralised, e.g. by means of lime.

Dioxins are highly hydrophobic. They also attach to all surfaces, including those of fly ash. In old, obsolete incinerators typically 85% of dioxins report to fly ash, and quite conveniently are arrested by baghouse filters. However, the balance (15%) still exceeds the extremely low regulatory limit value, typically 0.1 ng TEQ/Nm^3 (in China 1 ng TEQ/Nm^3). Hence, to adsorb all dioxins 50-200 mg /Nm^3 Activated Carbon (A.C.) is injected. Both the injection and dispersion of A.C. in the flue gas and flue gas filtration in the baghouse must be well designed, operated and maintained.

6. Corrosion

Most corrosive gases attack steel. Combustion of MSW generates a highly corrosive environment composed of gases and ash and laden with HCl, SO_2, NaCl, KCl and heavy metal chlorides and (subsequently) sulphates. Corrosion rates rise with temperature and – depending on metal structure and composition – diminish by formation of protective layers. Coherent consideration of corrosion processes is difficult, as physical, chemical, operational, metallurgical and crystallographic parameters interact and the precise origins of corrosion vary from case to case, are multiple and generally difficult to identify. Thermodynamically speaking, some extent of corrosion is unavoidable. Countermeasures may help to reduce corrosion damage to acceptable levels. These require both constructive and operational counter-measures. Low steam parameters in the boiler system, long residence and reaction times (for sulphatation of chlorides) before entering in contact with convective heat surfaces, lowering the flue-gas speed, and levelling of the speed profile may all be successful. Protective shells, tooling, stamping, and deflectors can also be used to safeguard heated surfaces.

A compromise must be found in determining the boiler cleaning intensity between best possible heat transfer (metallic pipe surface) and optimal corrosion protection.

Currently, corrosion phenomena are particularly observed on superheater tubes. The key role of formation of a molten phase, obviously related to ash composition and flue gas temperature as well as to the deposit morphology, is related to the flue gas flow pattern, to the mechanisms and corrosion rates. A theoretical analysis and enumeration of corrosion's numerous forms and appearances is given in the E.U. *Reference Document on the Best Available Techniques for Waste Incineration* [1].

6.1. Forms of Incinerator Corrosion

In the fifties and sixties Germany built numerous large-sized MSWI plants. Refuse was assimilated then to fuel free of charge and the first generations of plants were designed to squeeze a maximum of power from this resource. Soon, severe corrosions were encountered and their sources analysed; several major areas of concern were identified:

- Severe corrosion occurred in integrated boilers, affecting mainly the lower half of the boiler tubes surrounding the combustion chamber. This form of corrosion derives from **alternating oxidising and reducing conditions**, which prevent protective and coherent oxide films to form. It proceeds through $FeCl_2$-formation under deoxygenated flue-gas atmosphere, e.g. under oxide films, contamination or fireproof material especially in the furnace area. $FeCl_2$ is sufficiently volatile at these temperatures and therefore mobilised. An indicator for such conditions is the periodic appearance of CO. Corrosion products appear in flaky layers. Today, this part of the boiler is clad with protective refractory, often thermally conductive silicon carbide.
- High temperature **superheater corrosion**. In synergy with other factors, such as inappropriate boiler design and tacky deposits accumulating on superheater tube banks, hydrogen chloride and chlorine play a major role: chloride is released during sulphating of alkaline chlorides, and attacks iron. Corrosion is observed in MSWI with flue-gas temperatures >700 °C and at pipe wall temperatures above 400 °C. The corrosion products form a black firmly bonded cup that includes a hygroscopic red $FeCl_3$ layer in thicker films.
- **Molten salt corrosion**: flue-gas contains alkali, which forms low-melting salts and eutectics. Such molten systems are highly reactive and cause severe corrosion or even react with refractory lining and destroy it mechanically.
- **Standstill corrosion** creates problems after a shutdown, whether scheduled, or not. $CaCl_2$ deposits are hygroscopic, some heavy metal chlorides may even hydrolyse, liberating free HCl. Electric tracing is often required to keep such deposits dry.
- **Dewpoint corrosion** is associated with acid gases that condense at the cold, rear end of the boiler.
- Superheaters may suffer damage from erosion due to excessive flue gas approach velocities and/or soot blowing. Such soot blowers are difficult to adjust: if the jets blow too hard it causes erosion; if too soft, it is useless.

6.2. Sulphatation

Salts and metal chlorides sublimate at furnace temperature, leaving a cleaner remaining residue. In the first boiler passes the temperature remains above 650°C and ash is still tacky. Below 600°C, the flue gas may contact tube banks, without excessive risk of fouling these. Nevertheless, tube deposits will form by non-sticky particles separated by inertia and interception. These deposits also collect chloride salts. Thermodynamically, the latter are no longer stable, as they were at furnace temperature. In contact with SO_2 they are gradually converted into sulphates according to reactions such as:

$$MeCl_2 + SO_2 + \frac{1}{2} O_2 = MeSO_4 + 2\,HCl \qquad (Me = \text{bivalent metal})$$

Such reactions actually consolidate and harden deposits. Moreover, while liberating HCl they contribute to corrosion processes, with HCl being slowly oxidised to Cl_2 that diffuses to the tube metal and attacks it; once it is reduced to HCl the same corrosive cycle starts over again. From this viewpoint, it is favourable that the flue gas is rich in SO_2, so that sulphatation proceeds even before salt laden dust is deposited on the tubes.

6.3. Boiler design

The design of a boiler mainly depends on steam quality (boiler pressure + superheat temperatures), water circulation requirements (MSWI boilers feature natural convection) and flue-gas characteristics (corrosion, erosion, and fouling potential). When selecting steam parameters for waste fired boilers a compromise is searched between yield of power generation and superheater lifetime: an operating pressure of 40 bar (4 MPa) and 400 °C are common choices when power is generated, although higher values are sometimes selected. Corrosion becomes more severe, as steam temperature increases. Steam superheaters are especially vulnerable, since they operate at the highest temperatures of the steam circuit and are hence located at the high temperature side of the boiler; moreover, their internal cooling is low-grade (pressure steam, stead of boiling water). Corrosion-resistant materials and coatings are key to increased conversion efficiency and reduced maintenance in waste-to-energy (WTE) plants. Another possibility is to heat the steam superheater in a separate, natural gas or oil-fired furnace.

During the sixties, boilers were designed according to conventional rules: compact, high rate of heat transfer sustained by relatively high linear gas velocities. This design was at the source of failures: some superheaters, designed for 20,000 operating hours, barely reached 3 to 4,000 hours: settings for improved heat transfer also created conditions leading to rapid fouling or even clogging of tube banks and to rapid corrosion! From the seventies, some simple rule-of-thumbs emerged that led to large-volume, inefficient boilers, however, without the operating problems cited afore:

- Convection surfaces in the boiler passes are placed only after 1, 2, or even 3 empty boiler passes, so that the flue gas temperature is lower than 600 or at most 650°C. In this temperature range, fly ash no longer remains tacky.
- The clearance between superheater tubes is large and the approach velocity is low (few ms^{-1}) limiting inertial fly ash deposition.
- Deposited fly ash is periodically removed using steam jets or dropping shot onto tube banks.

Chlorides, chlorine, and hydrogen chloride play an important role in some forms of corrosion. Yet, also other factors play a synergetic and decisive role, often related to the creation of electrochemical cells with at one side tube metal, at the other deposits. Rate controlling is not the amount of chlorine in the system, but the electric conductivity of the deposit layer. Basically, molten phases must be avoided. Avoiding PVC still leaves KCl and NaCl, mainly present in the vegetal part of MSW and does not solve the superheater corrosion problem.

7. GREENPEACE

Greenpeace is a non-governmental environmental organisation, which uses spectacular direct action, lobbying and research to achieve its goals, namely to "ensure the ability of the Earth to nurture life in all its diversity". Today Greenpeace focuses on worldwide issues, such as global warming, deforestation, overfishing, commercial whaling and nuclear power. Campaigns of Greenpeace have raised environmental issues to public knowledge and influenced both the private and the public sector. Typical Greenpeace papers are cited as internet entries. The issue of treating potable water by chlorination seems to have internally split the organisation. http://en.wikipedia.org/wiki/Greenpeace today no longer mentions keywords such as incineration, PVC, or dioxins. Still, by its actions Greenpeace contributed positively to the cleaning of incinerator flue gas to the present stringent standards, as well as to responsible proactive initiatives in chemical industry at large and the PVC producers in particular.

Numerous assertions from Greenpeace were exaggerated, if not incorrect; their vigorous campaigns and actions against incineration have caused unwarranted negative publicity to the sectors of incineration, chlorine, and PVC production and conversion. Yet, still now, numerous people believe incineration to be an undesirable and grossly polluting activity. This popular belief considerably complicates the planning and licensing of new incinerator plant, at a time that almost all major Cities in China are surrounded by a suffocating girdle of landfills. An undesirable consequence of this state of affairs is that the paucity of legal and duly controlled incineration plant paves the way to open burning and illegal and uncontrolled combustion of waste causing much higher harm!

8. VINYL 2010

Some pressure groups demanded (and at times still demand) restrictive measures on the uses of PVC and/or some of its additives. Since such issues no longer pertain to rational decision-making there was lots of confusion in the E.U. with its climax in the years 1998-2000. Confronted to a file of great complexity of these issues on the one hand (the applications and formulations of PVC are quite varied), public pressure on the other, the E.U. decided to launch a number of studies focusing on the uses, virtues and eventual hazards of PVC [9]. PVC Industry (resin and additives producers, converters) decided to take a new initiative, shaped as a Voluntary Commitment with precise objectives and timetable [9]: Vinyl 2010 was born. At present and despite an unfavourable economic background, it seems that it will keep all its promises, while ensuring complete transparency:

- The production of suspension and emulsion PVC is inspected and monitored and its footprint reduced.
- Additives containing cadmium were phased out and those containing lead are in the process of phasing out.
- Risk assessment studies have been conducted for all major plasticisers and assessed by scientific panels.
- The target of recycling 200,000 tonnes/annum of non-regulated post-consumer PVC is closely approached.

Industry intends to continue these efforts setting new goals for 2020 (www.vinyl2010.org/).

9. Prospects and Conclusions

This paper tells the story of Incineration and PVC.

Popular pressure against incineration as a modern and responsible elimination method of MSW (and other residues) is entirely unfounded in the E.U., given the demanding emission standards and their strict enforcement. In China, controls over dioxin and other emissions are being increasingly implemented and in few years China will satisfy the same strict standards as the E.U., including those related to monitoring emissions and inspection [2].

By and large, most operators do not perceive PVC as a problem in MSW incineration. It contributes to the heating value of MSW and already at low temperature looses almost all chlorine as HCl. In principle, HCl can be recovered and used to extract heavy metals from fly ash. Even though PVC enhances the concentration of HCl in flue gas, there is no evidence that things would notably improve in its absence: also without PVC superheater corrosion will take place and dioxins will still be formed and destroyed. Chlorine's contribution to the creation of dioxins is marginal in MSWI and negligible compared to other, more important factors of influence, such as set ups in combustion, hot ESPs, and the creation of catalysts assisting in chlorination and low temperature catalytic oxidation of carbon, i.e. in the *de novo* route of formation.

Flue gas cleaning is in any case essential in limiting the emissions from Municipal Solid Waste Incineration. PVC augments the amount of neutralisation salts for disposal. In the E.U. one of the better and cheaper solutions is to return these in the salt mines, which supplied salt for their creation. Technologies are also being developed to recycle these residues.

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