Power Plant[1] Emissions during Startup and Shutdown
Biofuelwatch briefing, September 2014

When power plants are started up and shut down, emissions of several air pollutants have been found to spike, sometimes dramatically so – especially during startups. Sub-optimal combustion temperature can cause much greater emissions, but emission spikes nonetheless happen when auxiliary gas or diesel boilers are used to achieve the desired temperature before any solid fuel is burned. One of the causes is the 'memory effect', whereby dioxins and furans are adsorbed onto scrubbers and then released under stable combustion conditions. However, not all of the reasons for emissions spikes during those periods are fully understood.

Most of the scientific studies on this have focussed on Dioxin and Furan and well as Polycyclic Aromatic Hydrocarbon emissions during power station startup and shutdown. Those show particularly dramatic spikes during those periods.

However, other emissions, including NOx emissions, also peak during power station startup and many Air Pollution Control Devices do not work until several hours after electricity generation has restarted following start-up and then take more hours to work as effectively as during continuous operation. And electricity generation can only (re)start several hours after solid fuel combustion has (re)commenced.

Any power plant requires routine shutdowns for maintenance several times a year. However, when a new power station, or one newly modified, for example to run on biomass rather than coal is commissioned, there will be a 'test' or commissioning phase. During this period, which can last for several weeks or months, there will be far more frequent shut-downs and startups than during later smooth operation. Thus, during the commissioning phase, emissions of several pollutants can be expected to be significantly greater per volume of fuel burned than at other times.

Evidence from peer-reviewedstudies:

- Characteristics of dioxin emissions at startup and shutdown of MSW incinerators, Hajime Tejima et al, Chemosphere 66 (2007), 1123-1130

  Summary of key findings:
  The study looked at the operation of a Japanese incinerator with very low levels of dioxin emissions during steady state operation (0.006ng WHO-TEQ $Nm3^2$). For startup, an auxiliary burner was used and waste incineration was only started once combustion gases reached a temperature of more than 750°C. Average dioxin emissions during the startup process were 1.9 ng WHO-TEQ Nm3 and average emissions during shutdown were 0.72 ng WHO-TEQ Nm3. Four startup periods combined accounted for 41% of total annual dioxin emissions. Contamination of ash with dioxins was also increased during startup.

  Abstract:
  "Dioxin concentrations from municipal waste incinerators in Japan and elsewhere often show low concentrations that comply withlegal limits (in this paper, the term ''dioxin'' designates WHO-TEQ: PCDD/Fs + dioxin-like PCB). However, such data is usually generated under normal steady state operational conditions, and there has been little investigation of releases occurring during startup and

[1] Please note that this briefing relates to power stations and incinerators that burn solid fuel, i.e. directly combusting biomass, coal or municipal solid waste. It does not look at gas-fired turbines.

[2] The toxicity of dioxin emissions is expressed as Toxic Equivalency or TEQ and the World Health Organisation (WHO) sets a standard for measuring TEQ.

shutdown. It is important, therefore, to ascertain quantitatively emissions in an unsteady state (startup and shutdown) in order to correctly evaluate the relationship between emissions from a facility and the surrounding environment. The present study aimed to examine dioxin emissions of a continuously operated incinerator at startup and shutdown, and estimating the time period of greatest emission, and the processes causing dioxin generation.

The startup process was divided into five stages and the shutdown into two; at each stage, dioxins in the flue gas were measured at the boiler outlet and the stack. From the concentration of dioxins and the flue gas volume at each stage, the amount of dioxins at startup and shutdown were calculated, and these were compared with that under steady state conditions. Dioxin concentration at the stack under steady state conditions was a very low level, while those at startup and shutdown were higher.

In the case where dioxin concentration under a steady state is a low level like in this study, it is indicated that the total annual dioxin emission from a facility could be attributed to the startup periods."

- Influence of start-up on PCDD/F emission of incinerators, Lin-Chi Wang et al, Chemosphere 67 (2007) 1346-1353

Summary of key findings:
This study looked at five waste incinerators in Sweden. It found that a single startup operation could emit 60% of the annual dioxin and furan emissions for a whole year of normal operations. Dioxin and furan emissions were up to 860 times greater during startup than during long-term steady operation. Even when steady operation was achieved after a startup, emissions could still be as much as two or three times higher than normal.

Abstract:
"This study aims to evaluate the influence of start-up on polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) concentration in the stack flue gas of incinerators and its contributing PCDD/F emission. The PCDD/F emission of the first sample among three consecutive stack flue gas samples of five intermittent incinerators, which sampled at a stable combustion condition after start-up, is 2–3 times higher than the mean of the others. For verifying the PCDD/F characteristics of incinerators during start-up, one continuous MSWI was investigated for two years. The elevated PCDD/F emissions of the MSWI during start-up could reach 96.9 ng I-TEQ N m^{-3} and still maintained a high PCDD/F emission (40 times higher than the Taiwan emission limit) even 18 h after the injection of activated carbon, indicating the memory effect. Taking the MSWI for example, which consists of four incinerators, the estimated annual PCDD/F emission from normal operational conditions was 0.112 g I-TEQ. However, one start-up procedure can generate ~60% of the PCDD/F emissions for one whole year of normal operations. And the PCDD/F emission, which is the result of the start-ups of four incinerators, was at least two times larger than that of a whole year's normal operations, without consideration for the PCDD/F emission contributed by the long lasting memory effect."

- Polynuclear aromatic compounds in flue gases and ambient air in the vicinity of a municipal incineration plant, Anders L. Colmsjö et a, Atmospheric Environment, Volume 20, Issue 11, 1986

Abstract:
"The levels of concentration of polynuclear aromatic compounds (PACs) in the stack gases from a municipal incineration plant were determined on eight

occasions during a period of 1 week. Low levels of emitted PAC were recorded during days of normal operation, in contrast to the day when cold start-up of the plant occurred, the PAC levels being consequently increased by more than a 1000-fold. Air particulate PAC levels in an adjacent suburb were monitored, both simultaneously and over an extended period of time."

[Note:PACs are a group of chemical compounds which include Polycyclic Aromatic Hydrocarbons or PAHs. A significant number of PAHs are toxic to humans.]

- Emission of Nonchlorinated and Chlorinated Aromatics in the Flue Gas of Incineration Plants during and after Transient Disturbances of Combustion Conditions: Delayed Emission Effect, R Zimmermann et al, Environ. Sci. Technol., 2001, 35 (6), pp 1019–1030

  Summary of Key findings:
  This study looks at the effects of 'disturbed combustion conditions', including startups on dioxin and furan and on PAH emissions from waste incinerators. It found that after a short period of disturbance, emissions could be increased over a lengthy period.

  Abstract:
  "The profiles of different products of incomplete combustion (PIC) in the flue gas of a 1 MW pilot combustion facility were investigated under normal steady-state and disturbed combustion conditions. The behavior of emission profiles after disturbed combustion conditions was investigated in order to obtain a better understanding of emission memory effects. Highly time-resolved, quantitative on-line measurements of several aromatic species down to low ppbv or higher pptv concentrations were performed by a mobile resonance-enhanced multiphoton ionization time-of-flight mass spectrometer. Conventional analytical methods (gas chromatography−mass spectrometry and high-performance liquid chromatography) were also applied for measurement of polycyclic aromatic hydrocarbons (PAH) and polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/F). The sampling point was located in the high-temperature region of the plant at the outlet of the post-combustion chamber at temperatures between 650 and 880 °C, prior to any emission reduction devices. The investigation pointed out that after a short phase of disturbed combustion conditions, e.g., due to process changes, transient puffs, or malfunctions, the composition of combustion byproducts in the flue gas can be changed drastically for a very long time ("memory emission" effect). It is suggested that carbonaceous layers, deposited on the inner walls in the high-temperature zone of the plant, might be responsible for the observed memory emission of some PAH species. Drastic changes in the profiles of the PCDD/F homologues were also observed during memory emission conditions. The PAH memory most likely is due to pyrolytic degradation of the carbonaceous layers, while the altered PCDD/F homologue pattern may be mediated by the high catalytic activity of the freshly formed deposit layers. Finally, it should be emphasized that a rich pattern of aromatic species, including PCDD/F, was found in a temperature regime well above the typical temperature window (≈300 °C) for de novo PCDD/F formation."

- PCDD/F and PCBz Emissions during Start-up and Normal Operation of a Hazardous Waste Incinerator in China, Xiaoqing Lin et al, Aerosol and Air Quality Research, 14: 1142–1151, 2014

  Abstract:

"The PCDD/F[3] emissions from incinerator start-up are a major contributor to the total amount of such emissions, as has been reported in studies of numerous municipal solid waste incinerators. However, very few studies have examined the start-up process at hazardous waste incinerators (HWIs). In this work westudied the emissions of PCDD/Fs and other pollutants, such as PCB[4]z, at the stack during start-up and normal operations in a HWI. We found that the PCDD/F emissions during start-up were greater than during normal operations, and were comparable to the annual emissions during the normal combustion regime. The emissions of PCDD/Fs were highest during start-up whenthe temperature was around 500°C, reaching 59.5 ng/Nm3(5.49 ng I-TEQ/Nm3) when no APCDs[5] were applied. The emission values of PCDD/Fs during start-up with the application of APCDs and during normal operations were very low, which indicates the importance of APCDs when starting up a HWI, as well as before feeding waste. The chlorination degree, the ratio of PCDFs/PCDDs and the congener profiles were also discussed during start-up and normal operations, with the results suggesting different formation mechanisms of PCDD/Fs. PCBz emissions are two or three orders of magnitude higher than those of PCDD/Fs, and 1,2,4,5-TeCBz was the best correlatedPCBz used as a PCDD/F indicator in real HWI flue gas."

Other evidence

- Assessment of startup period at coal-fired electric generating units, US Environmental Protection Agency, Office of Air and Radiation, Peter Kokopeli et al, June 2013
  The report examines the operation of Air Pollution Control Devices during power plant startup periods. It found that an average coal power station had 9-10 startups a year, however some had over 100 such events. 20% of startup attempts fail after fossil fuels have started to be combusted and then need to be repeated. On average, the period of time between a Pulverised Fuel plant starting to burn fossil fuels and starting to generate electricity is around 9 hours – for Circulating Fluidised Bed plants, it is longer, up to 75 hours in some cases. It then takes several more hours for a plant to operate at its normal capacity.

  Selective Catalytic Reduction, the most effective technology for reducing NOx emissions, does not work until 2-6 hours from when electricity generation has re-started and it then takes up to 14 hours further for NOx levels to drop to normal.

  Where Flue Gas Desulphuration is used to reduce SO_2 emissions, the technology does work by the time electricity generation restarts but SO_2 levels remain above normal for several hours (except for subcritical pulverised coal plants using wet flue gas desulphuration). Circulating Fluidised Bed plants generally do not use flue-gas desulphuration. Their SO_2 levels peak about three hours after generation starts and then gradually decline.

- Startup and Shutdown NOx Emissions from Combined-Cycle Combustion Turbine Units, Robert J. Bivens, RMB Consulting & Research Inc, May 2002
  Relevant quotes:
  "For any given combined-cycle unit with an ultra-low NOx permit limit typically ranging from 2–5 ppm NOx(or lower), it is an understood and accepted fact that the low NOxlimit is a steady-state, controlled limit made possible by proper combustion and control technology practices.

[3] Dioxin and Furans
[4] Polychlorinated Biphenols (banned globally since 1986 but still found in old products, hence a concern for hazardous waste incineration)
[5] Air Pollution Control Devices

Startup and shutdown emissions, on the other hand, are not steady-state emissions and are notcontrolled (i.e., from a control technology standpoint), and, as a result, are significantly higherand extremely more random than those emissions under controlled operation."

" The natural laws of physics and chemistry dictate that uncontrolled NOxemissions at levelssignificantly higher than NOxemissions at the steady-state, controlled level are impossible toavoid during startup and shutdown periods."

- Effects of Varying Combustion conditions on PCDD/F Formation, Johanna Aurell, Umea University, Sweden, http://www.diva-portal.org/smash/get/diva2:141996/FULLTEXT01.pdf

  This report confirms that dioxin and furan conditions can remain elevated for significant periods after interruptions to normal combustion conditions, such as startups.