

## INVESTIGATION INTO THE EFFECT OF ORGANIC NITROGEN COMPOUNDS ON THE SUPPRESSION OF PCDD/Fs IN IRON ORE SINTERING

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### Abstract

An experimental sinter box was used to compare the performance of solid urea, aqueous urea and monoethanolamine (MEA) as reagents for the suppression of PCDD/Fs in the iron ore sintering process. The addition of solid urea, aqueous urea or MEA, at 0.009% nitrogen equivalent, reduced the formation of total PCDD/Fs, targeted PCDD/Fs and PCDD/F I-TEQ by ~47-53%, 62-64% and 59-62%, respectively. However, a five-fold increase in addition of MEA led to significant reductions in PCDD/F suppression efficiency especially for total PCDD/Fs, where the efficiency fell to 11%. The addition of urea or MEA did not affect the number of PCDD and PCDF congeners and typically 70 to 72 PCDD/Fs were detected, of which 48-51 were PCDFs. It is concluded that there is no significant difference between the use of solid and aqueous urea and that the use of MEA offers no advantages over the use of urea. At an industrial scale, the use of aqueous urea could alleviate handling problems experienced with solid urea arising from its hygroscopic nature.

### Introduction

Studies conducted by Corus<sup>1,2</sup> showed that the iron ore sintering process is the only noteworthy source of PCDD/Fs in the integrated steelmaking process, and that formation may be partially suppressed by the addition of small amounts of urea to the sinter feed mixture<sup>3-6</sup>. This led to longer term proving trials to confirm that there were no adverse effects of using urea continuously in a production scale sintering plant. Typically it was found that the addition of 0.02% urea to the sinter feed mixture reduced dioxin emissions by about 50%. However, problems were experienced with feeding of solid urea owing to its hygroscopic nature, which led to bridging of the material in the storage silo and blockages in the feeding system. The use of a liquid reagent for suppression should obviate the handling problems found with urea and therefore studies have been carried out using an experimental sinter box to evaluate the performance of aqueous solutions of urea and monoethanolamine (MEA) for dioxin suppression in the sintering process.

### Materials and Methods

#### Experimental sinter box apparatus

The sintering of iron ore is an essential stage in the so-called integrated steelmaking process and its main purpose is to prepare fine ores for use in the blast furnace. The sintering process is operated under tight control and it is therefore not possible to examine the influence of wide changes in raw mix composition or variations in the process conditions on production plants. The experimental sinter box is a small-scale system that allows the industrial-scale process to be simulated in the laboratory. The sinter box was developed principally for use in studying the sintering characteristics of different ores and ore blends prior to use at industrial scale and it is well established for this use worldwide. In recent years the sinter box<sup>7</sup> has been shown to be applicable to studies on the generation and suppression of trace organic emissions from the process. A major advantage of using the sinter box for environmental studies is that it permits sintering process conditions to be varied outside the tight constraints under which full-scale plants are operated, without adversely affecting sinter quality or productivity and without any risk of exceeding environmental emission limits. The cost of trials to evaluate new process variations at the sinter box scale is relatively inexpensive compared to industrial-scale trials.

The sinter box used in the experiments is essentially a small pilot plant that permits a sample charge of ~ 80 kg of raw sinter mixture, containing blended ores, fluxes and fuel, to be sintered in batch firings. The sample volume is cylindrical in shape and has a cross-sectional area of ~ 0.1 m<sup>2</sup> and a bed depth of ~ 500 mm. The sinter mixture is packed around the edges with a high grade iron ore to reduce heat losses by minimising air flow at the edges. The mixture is ignited using a propane gas burner located above the bed and, once the fuel particles at the surface have been ignited, the burner is extinguished and the flame front is propagated by drawing air through

the bed with a fan. Typically each firing takes ~ 30 mins and three or four test firings were run on each test mixture in a single day.

#### Raw mix preparation

On each day of operation, sufficient mixture was prepared for four test firings by mixing the raw materials in a drum mixer/pelletiser, together with the requisite amount of water to achieve a blend moisture content of ~ 7% by weight. The resulting micropellets were loaded into the sinter box and fired as described above.

#### Sinter mixture composition

All of the test firings were made using a base mixture that contained five high-grade iron ores in the same relative proportions and the blend composition was adjusted by the addition of limestone and olivine to achieve a lime:silica ratio of 1.60 in the product sinter. Coke breeze was employed as fuel at an overall addition rate of 3.3% by weight. Potassium chloride (75 g) was added to each mixture to give a constant level of chloride in the blend. A series of five experiments was carried out as indicated in Table 1.

**Table 1. Details of experimental programme**

Experiment No.	Details
1	Base sinter mixture
2	Base sinter mixture + 0.02% solid urea
3	Base sinter mixture + 0.02% urea (added as an aqueous solution)
4	Base mixture + 0.042% MEA
5	Base mixture + 0.21% MEA

#### Sampling method

Emission samples were collected by use of a UKAS-accredited method (ISO17025) based on US EPA Method 23. The sampling system, a Graseby Andersen Manual Stack sampling train (Graseby Andersen, Bedfordshire, UK), was composed of a heated glass-lined sampling probe and filter and a water-cooled XAD-2 sorbent trap. Samples were collected isokinetically through the heated glass-lined sampling probe, particulate were collected on a glass fibre filter contained in a heated filter box whilst vapour phase PCDD/Fs were trapped on XAD-2 resin contained in a water-cooled trap. XAD-2 sampling kits were pre-spiked with PCDD/F sampling standards (Cambridge Isotope Laboratories, LGC Promochem, UK). The analytical samples consisted of the filter, XAD-2 resin, and solvent washings from the glassware of the sampling train.

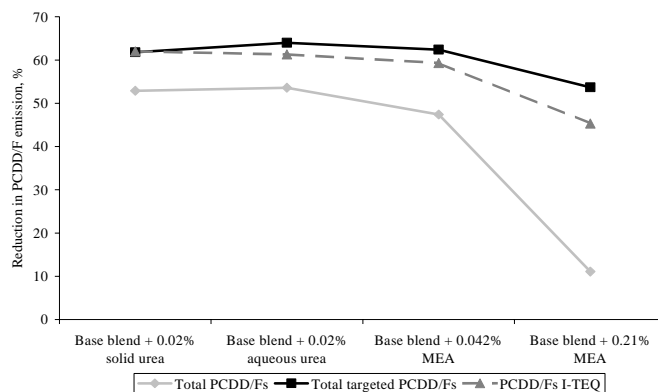
#### Analytical procedure

Samples were analysed in-house according to UKAS-accredited methods (ISO17025), described in more detail elsewhere<sup>8,9</sup>. Briefly, samples were spiked prior to extraction with the <sup>13</sup>C<sub>12</sub> internal standard solutions of the methods US EPA 23 and 1668A (Cambridge Isotope Laboratories, LGC Promochem, UK). Samples were extracted with toluene by accelerated solvent extraction (150°C, 2000 psi) using a Dionex ASE 200. Multi-layered silica chromatography columns were used for the initial clean-up of total extracts, Florisil chromatography was used to separate PCDD/Fs from PCBs. Recovery standards were added to the final PCDD/F fraction (Cambridge Isotope Laboratories, LGC Promochem, UK) prior to analysis by high resolution gas chromatography - high resolution mass spectrometry (HRGC-HRMS) on a Hewlett-Packard 6890 gas chromatograph fitted with a 60 m x 0.25 mm x 0.25 µm DB5-MS capillary column and coupled to a Micromass Autospec Ultima high resolution mass spectrometer. The MS was operated at 10,000 resolution in the positive ion mode at 34 eV energy with perfluorokerosene as the mass range calibrant.

## **Results and Discussion**

The results are summarised in Fig. 1, which shows the efficiency of reduction in emissions of total PCDD/Fs, total targeted PCDD/Fs and PCDD/F I-TEQ for the various reagents. It may be seen that there appears to be no significant difference between the use of solid urea (prills) and aqueous urea with regard to the suppression of total PCDD/Fs, total targeted PCDD/Fs or PCDD/F I-TEQ. With the addition of 0.042% MEA (equivalent to 0.02% urea on a nitrogen-equivalent basis) the PCDD/F suppression efficiency was broadly similar to that of

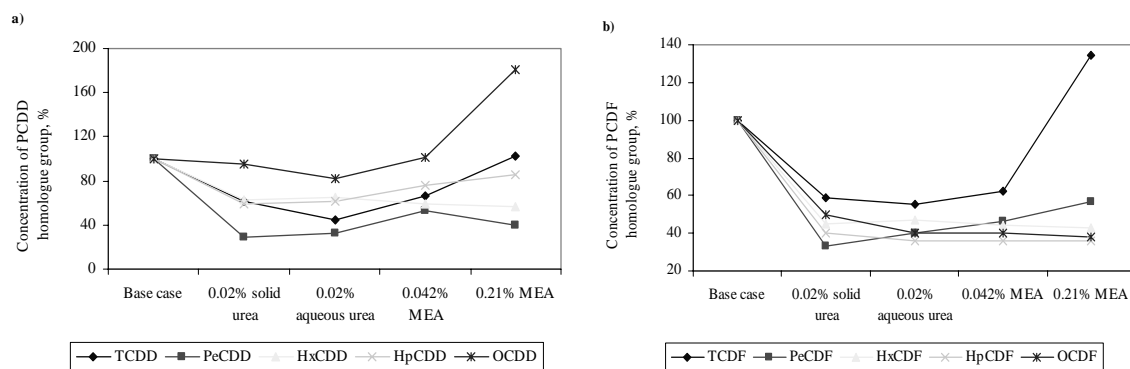
urea with respect to total targeted PCDD/Fs and PCDD/F I-TEQ but poorer for total PCDD/Fs. However, when the MEA addition was increased 5-fold to 0.21%, the PCDD/F suppression efficiency was markedly reduced, especially for total PCDD/Fs where it fell to 11%.



**Fig. 1. Variation in PCDD/F suppression efficiency with different reagents and reagent addition rates**

#### Effect of urea and MEA on homologue group profiles

The number of congeners detected within each homologue group remained effectively constant in each experiment, thus showing that the addition of urea or MEA as suppressant did not change the numbers of compounds formed in each homologue group. In the PCDD profile the concentrations of TeCDDs, PeCDDs and HxCDDs were reduced to a similar extent by use of either urea or MEA (Fig. 2a). However, HpCDDs and OCDD were not as effectively suppressed with MEA as they were with urea. The HxCDFs, HpCDFs and OCDF were suppressed to the same degree by solid and aqueous urea and by 0.042% MEA, but MEA was slightly less effective than urea in suppressing the formation of TeCDFs and PeCDFs (Fig. 2b). Moreover, when the MEA addition was increased from 0.042% to 0.21% there were significant increases in the amounts of TCDFs and PeCDFs formed, but the concentrations of the higher homologues remained effectively constant.



**Fig. 2. PCDD/F homologue group concentration profiles for each experiment**

#### Effect of urea and MEA on targeted congener profiles

The congener profiles for targeted PCDFs reflected those exhibited by the PCDF homologue group profiles. The targeted HxCDFs, HpCDFs and OCDF were all suppressed to more or less the same extent regardless of whether solid urea, aqueous urea, 0.042% MEA or 0.21% MEA was used. However, the concentrations of 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF were increased by factors of 1.98, 1.54 and 1.39, respectively, when the MEA addition rate was increased from 0.042% to 0.21% (Fig. 3). The homologue group concentrations of TeCDFs and PeCDFs were increased by factors of 1.96 and 1.42, respectively, when the MEA

addition was increased from 0.042% to 0.21%. This suggests that the increases in TCDF and PeCDF concentrations occurs to the same extent to all of the isomers in a given homologue group.

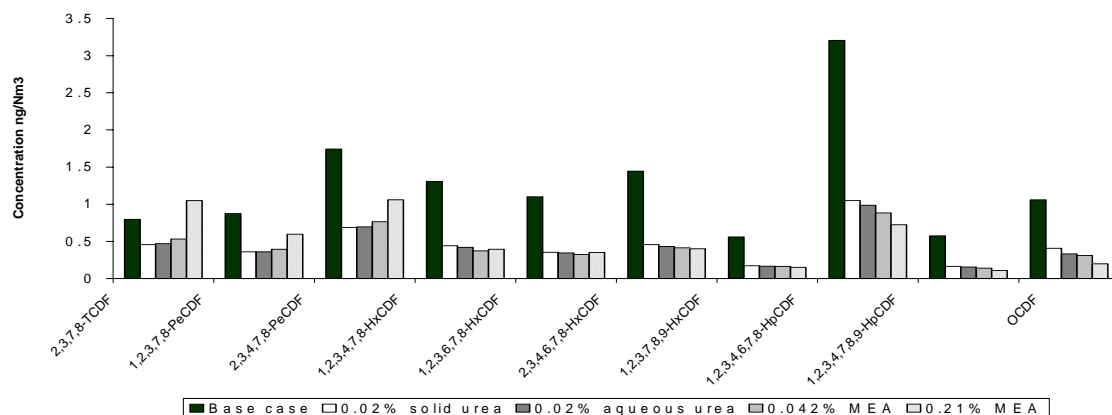


Fig. 3. Targeted PCDD/F concentration profiles for each experiment

#### Relative merits of solid urea, aqueous urea and MEA as PCDD/F suppressants

It has been demonstrated in previous extensive studies carried out by Corus<sup>3-5</sup>, that the optimum addition rate for suppression of PCDD/Fs using solid urea is 0.02 to 0.025% with respect to the sinter feed rate, which is equivalent to a nitrogen addition rate of 0.009%. Increasing the urea addition rate beyond the optimum level provides no further increase in PCDD/F suppression. Moreover, there are indications in industrial scale measurements that the suppression efficiency actually reduces at post-optimum addition rates. The results obtained in the present work show that there is little to choose between the performances of solid urea, aqueous urea and MEA when these reagents are added at a nitrogen equivalent of 0.009% (0.02% urea or 0.042% MEA). There would appear to be no benefit from using MEA instead of urea for suppression of PCDD/Fs in the sintering process. However, the use of aqueous urea could potentially overcome handling problems that have been experienced with solid urea. These problems may be attributed to the hygroscopic nature of urea, which can lead to aggregation of the urea prills during storage and feeding. In extreme cases such problems have resulted in bridging of material in a storage silo and fracture of a steel screw in a screw feeder system. However, the use of aqueous urea would require care since the moisture content of the sinter mix moisture affects the bed permeability. It would be necessary, therefore, to take into account the effect on the blend moisture of adding aqueous urea to the mixture. This in turn would determine, inter alia, the strength of the urea solution and the storage capacity required.

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#### References

1. Anderson D.R., Fisher, R., Chemosphere, 2002, 46, 371-381.
2. Fisher R., Anderson D.R., Pearson S.L. Quinn, P., Organohalogen Compounds, 1997, 31, 262-267.
3. Southern S M, Hakimian M, Edmundson J. *Proceedings of the 4<sup>th</sup> European Coke and Ironmaking Congress*, Paris 2000; 380.
4. Anderson D R, Fisher R, Roworth M C, Wilson D T, Southern S M, Fray T A T. *Organohalogen Comp* 2001; 54:110.
5. Anderson D R, Fisher R. *The Year-book of the Coke Oven Managers' Association* 2003; 163.
6. Fisher R, Fray T A T, Anderson D R. *ICSTI/Ironmaking Conference Proceedings* 1998; 1183.
7. Fisher R, Garcia Carcedo F, Alvarez Alaiz E, Pietruck R. European Commission Technical Report EUR 21429 EN.
8. Fisher R, Anderson D R. *Proceedings of the 48<sup>th</sup> British Steel/BISPA Chemists' Conference*, Scarborough, UK, June 12-13, 1996.
9. Wang, T., Anderson, D. R., Thompson, D., Clench, M., and Fisher, R., Chemosphere, 2003, 51, 585-594.