

DSC AND TGA STUDY OF DE NOVO ACTIVITY AND INHIBITION CASE STUDY: A MANGANESE ORE FINES SINTERING PLANT

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Introduction

According to the 'de novo' theory of dioxins formation a wide range of chlorinated aromatics are simultaneously formed as by-products of a catalytic, low-temperature combustion of carbon. At higher temperature these by-products are almost completely oxidised. Several research teams studied the problem and de novo activity is indeed indicated and quantifiable by various tests, including TGA, DTA and DSC. In this paper DSC-techniques are used to analyse samples, originating in a manganese ore fines sintering plant. The latter forms a special case in dioxins generation, because it unexpectedly proved capable of high dioxins emission levels, despite of very low chlorine and copper content of the ore, as well as limited cycling of both elements.

Six samples from March 2002 TEMCO Trials were DSC-analysed, to assess de novo activity via the heat effect associated with catalytic carbon combustion. A test reference sample (Merck Activated Carbon), three coarse ESP dust samples, and two fine ESP dust samples are DSC-tested, together with a sample of ore fines. The reference sample shows a gradual oxidation of carbon, rapidly escalating with temperature from about 400 °C upwards. The other samples show a similar behaviour, augmented for fine ESP dust with a catalytic oxidation starting at about 340 °C, for a de novo reaction a rather high starting temperature. The coarse samples show the same reaction but to an almost negligible degree, even more than in line with their much lower load of PCDD/F. One active sample is DSC-tested with 4 different inhibition treatments. Blank inhibitor samples are also tested. It is concluded that DSC allows differentiating samples according to the availability of carbon, activated by catalytic metal for low-temperature combustion.

Methods and Materials

Stieglitz et al.¹ described the DSC-method in detail, as applied to six dust samples, three blanks, four synthetic samples, and four real, inhibited samples. The nature of the 6 samples tested and the active sample elected (Field 2 ESP, cleaning gas from the baking section) are discussed elsewhere.

Blank Samples. Three DSC-tests are conducted: **NaOH**, **lime**, and **urea** are first brought onto a Florisil carrier, and then heated at a rate of 10 °C/minute.

Synthetic Mixture of Florisil, Activated Carbon, and CuCl₂·2H₂O. During a de novo test the effect of inhibitors was tested on a synthetic mixture (composed of 2g Florisil + 1 g activated carbon (AC) + 20 mg CuCl₂·2H₂O, added as both a chlorinating agent and a catalyst). The test was repeated with the same mixture, but adding 0.5% NaOH, 5% Ca(OH)₂, 5% urea (solid or liquid).

Inhibition of fine TEMCO ESP Dust. 5 tests were conducted, namely no addition (Base Case), addition of 0.5 % NaOH, of 5 % Ca(OH)₂, of 5 % urea (solid) and of 5 % urea (liquid).

Results and Discussion

DSC-Tests on Blank Samples. NaOH immediately upon heating shows loss of water, peaking at 104 °C and continuing for long. Lime, presents a gaussian, well-defined, endothermic dehydration peak at 441 °C ranging from 410 to 470 °C. Urea has two endothermic steps, at ca. 86 and 183 °C. For lime its dehydration temperature is probably too high to affect DSC-test results significantly. NaOH is only supplied in small amount. It is conceivable, however, that urea is already entirely decomposed in the DSC-test, before it can act as an inhibitor. In that case no effect will appear. According to Kirk-Othmer² urea decomposition starts at its melting point (132.7 °C) or higher, generating NH₃ and biuret NH(CONH₂)₂, triuret, heterocyclic cyanuric acid C₃N₃(OH)₃, and ammeline NH₂C₃N₃(OH)₂.

Mixture of Florisil, Activated Carbon, and CuCl₂·2H₂O, used as a synthetic model of filter dust.

- 1) **Effect on Carbon Oxidation.** This synthetic system is not inhibited by 5% urea, 0.5% NaOH or 5% Ca(OH)₂. Since these results do not conform to experience, the mechanisms of catalysis and inhibition of this synthetic model system may differ from reality on essential points.
- 2) **Effects on Fingerprints.** It is generally accepted that inhibition influences rates of formation, but not reaction mechanism. Indeed the fingerprints from the various tests show not much difference. Yet, lime addition gives a higher **ratio PCDD/PCDF** than the three other cases, and urea addition enhances the chlorination level, measured by the relative amount of OCDD and OCDF. Comparing fingerprint ratios, expressing the relative importance of 2,3,7,8-substituted congeners to their isomer group, is a critical test for change in formation mechanism. Only the PeCDD congener shows large variation, maybe by chance. All other ratios are virtually the same or show chance differences, as follows from their irregular, stochastic distribution over the 4 tests.

Chlorination efficiency for **PCDD** is as follows: Urea < Base case = NaOH < Ca(OH)₂
and for the **PCDF**: Ca(OH)₂ < Base case = NaOH < Urea

Level of chlorination, by and large, is always very high, demonstrating strong chlorinating power of 1 wt. % CuCl₂·2H₂O in the model mix. (Cf.)

The **PCDD/PCDF ratio** is definitely higher for the lime treatment. The toxicity reduction factor is rather high, especially when using urea. The formation of 2,3,7,8-substituted congeners is slightly less than standard.

DSC-Tests to mimic Inhibition of fine TEMCO ESP Dust

It is verified whether similar results can be attained using a DSC Test, confirming this test as a suitable means for inhibition studies:

Base Case, no addition. After initial moisture loss, the baseline starts mounting, even exponentially (slow carbon oxidation). From ca. 350 °C, a well-defined catalytic carbon oxidation peak develops, culminates at 430 °C, and ends at 480 °C. Then non-catalytic carbon oxidation takes over.

Adding 0.5 % NaOH. After a similar start there is marked endothermic loss of moisture between ca. 65 and 180 °C. then the peak of the former case is well reproduced. Thus, carbon oxidation is not inhibited, more or less as experienced in practice.

Addition of 5 % urea (solid). As for NaOH endothermic phenomena occur before de novo reaction even starts (**Figure 1**). The latter are possibly somewhat delayed start and with a reduced heat effect, mainly marked for the experiment with:

Addition of 5 % urea (liquid). Oxidation is somewhat inhibited. Evolved Gas Analysis could show whether there is a general inhibition of Volatile Organics formation, or rather a reactive conversion of chlorinated compounds into others, with inbuilt nitrogen resulting from urea decomposition.

Addition of 5 % Ca(OH)₂ (Figure 2): In contrast with all former cases, carbon oxidation takes an early start (288 °C, i.e. 60 °C earlier), but the later DSC-peak and its ending are as before. Nevertheless, peak surface is 30 to 50 % larger than in previous cases, with earlier carbon reactivity and a higher conversion as a cause. Thus, oxidation is not inhibited, but rather accelerated.

The previous **DSC-results** show that the peak temperature and end of de novo is unaffected by any of the additives tested. Still, lime really affects carbon oxidation, starting 60 °C earlier and heat generated increasing! Urea could lead to some delayed start, but the peak remains the same.

These values should now be compared to the real plant experiments.

Since the favourable results from the real scale tests are not confirmed, the validity of the method is questionable for inhibitors decomposing at low temperature, such as urea.

Conclusions

DSC is a useful method for rapidly verifying occurrence and extent of low temperature, catalytic oxidation of carbon, giving useful information on starting, peak and final temperature, and heat effects accompanying carbon oxidation as well as any other prior processes. For some applications Evolved Gas Analysis should accompany it, to identify the phenomena detected by heat effect.

This work aimed at establishing inhibitory effects from various usual inhibitors. A synthetic sample, composed of Florisil, Activated Carbon, and CuCl₂, and inhibitor blanks were also tested.

Thus the practical conditions of lime and NaOH dehydration were established, as well as the decomposition modes of urea. The latter varied for pure urea (solid) and dust sample with solid or liquid urea. There was no inhibition to be observed from NaOH and rather little at the side of urea. Possibly its decomposition, in this test procedure comes too early. Lime is remarkably active enhancing early carbon oxidation, which starts now ca. 290 °C instead of (a late) 350 °C.

References

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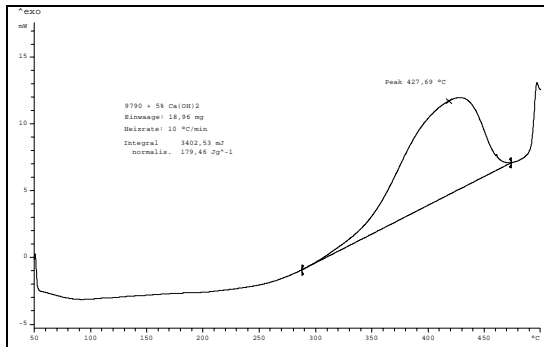


Figure 1. Sample with 5 % Ca(OH)₂ gives rise to an early start of *de novo* oxidation

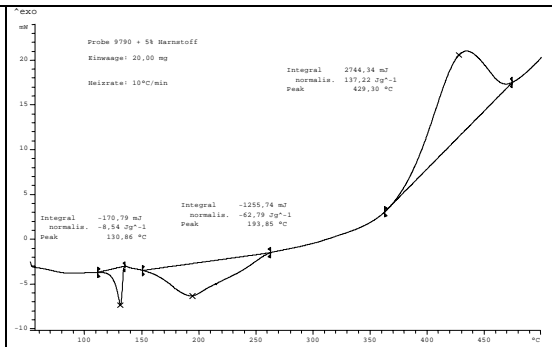


Figure 2. Sample with 5 % of Urea added, showing its early decomposition

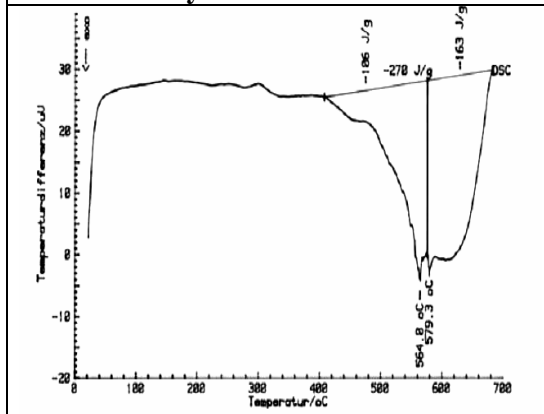


Figure 3. DSC-plot of iron ore sinter feed: oxidation starts > 400, peaks at 580 °C

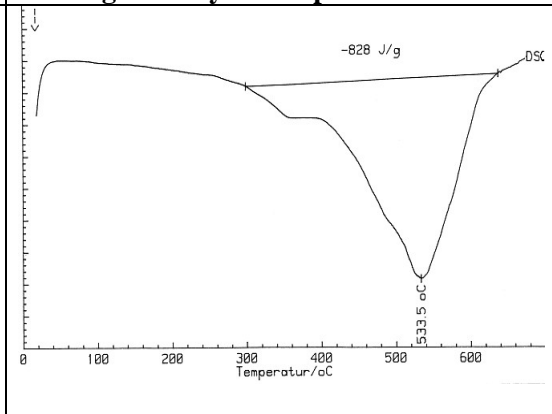


Figure 4. DSC-plot of ESP Field-1 Dust. Oxidation starts ca. 300, peaks at 533 °C

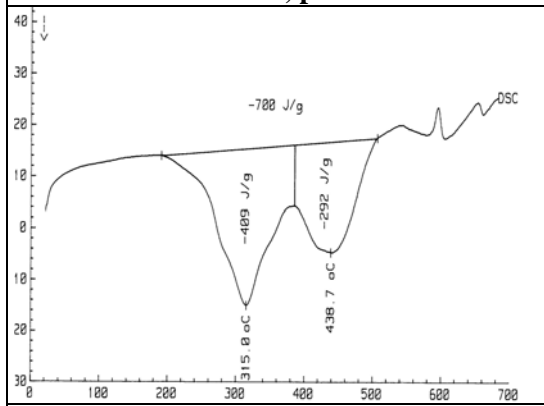


Figure 5. Oxidation in reactive field-2 dust starts < 200°C, peaks at 315 and 440 °C

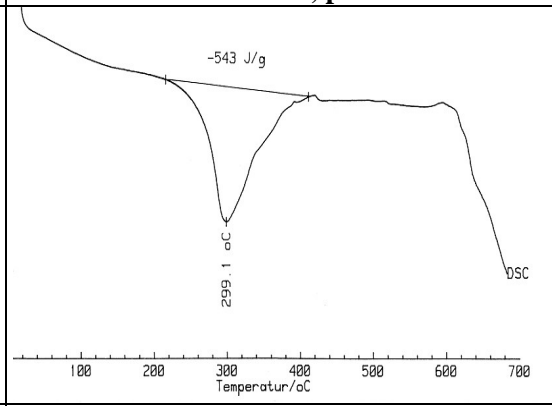


Figure 6. Oxidation in highly reactive field-3 dust peaks at 300 and ends at ca. 400 °C