

ENVIRONMENTAL EFFECTS OF COAL COMBUSTION

G. Hakvoort

DELFT UNIVERSITY OF TECHNOLOGY, CHEMISTRY DEPARTMENT, JULIANALAAAN
136, 2628 BL DELFT, THE NETHERLANDS

First an introduction is given about the environmental effects of coal combustion. Then the thermoanalytical research in this field is reviewed. Modern topics are the catalytic reduction of NO_x in exhaust-gases and the development of regenerative sulfur capture sorbents for use in fluidized-bed coal combustion.

Keywords: coal, combustion, environmental

Introduction

Coal is a very important source of energy [1, 2]. Normal fixed-bed combustion, however, gives a lot of environmental problems, caused by the ash and sulfur content and by the production of CO_2 and NO_x during combustion [2, 3].

Environmental protection demands low concentrations of SO_2 and NO_x in the exhaust gases, and only small amounts of solid residues.

An important NO_x source is formed by reaction of N_2 and O_2 from the air at the normally used high combustion temperatures (1400°C). This can be solved by application of fluid-bed combustion (FBC), proceeding at much lower temperatures ($800\text{--}1000^\circ\text{C}$). Further lowering of the NO_x concentration can be performed by reaction of the exhaust gases with NH_3 over an appropriate catalyst [4, 5].

Sulfur can be removed by reaction with, mostly CaO containing, sorbents. Often limestone (CaCO_3) or dolomite [$\text{CaMg}(\text{CO}_3)_2$] are applied. Uptake of sulfur proceeds up to about 1000°C , with formation of CaSO_4 . At higher temperatures this CaSO_4 will decompose again. This means that sorbents are active in FCC combustion, but not in combustion processes at higher temperatures. Then the sulfur has to be removed in the off-gas after cooling down.

A disadvantage of the use of limestone or dolomite is the fact that only a part of the calcium will react with sulfuroxide, owing to the formation of a tight shell of CaSO_4 on the surface of the sorbent particles. So the solid residue will contain ash, reacted sorbent and unreacted sorbent material.

Noordergraaf and van der Berg [3] give examples of the product streams for a FBC installation for continuous production of 600 MW electricity, using coal with 3% S and 15% ash.

Assuming an electric efficiency of 39% and a sorbent utilization (dolomite) of 65%, the following solid reactant and product streams are calculated:

coal	1.700.000 ton/year
dolomite	410.000 ton/year
residual ash	260.000 ton/year
residual sorbent	370.000 ton/year

As can be seen, the amount of solid residue is more than doubled by the application of sorbent material. This problem can be diminished by application of regenerable sorbent materials. Then the sulfated sorbent is separated from the coal ash and regenerated in a reducing atmosphere, by which gypsum is reduced into CaO and SO_2 . This SO_2 can be used for production of sulfur or sulfuric acid [3, 6, 7].

Research by Thermal Analysis

A good recent overview of a part of the discussed problems is given by Warne [8]. The processes, mentioned before, involve weight changes (uptake and release of sulfur oxides, combustion of coal), caloric effects (oxidation, reduction) and changes in gas-phase composition. So several thermal analysis techniques can be applied, for instance DTA/DSC [4, 5], EGA [4, 9, 10] and TG, this last technique being the most frequently used [6–22]. Often thermal analysis with variable atmosphere is applied, for separation of different effects.

The following types of investigations can be mentioned:

A. Development of specific thermal analysis equipment.

Since investigations are made in oxidizing, reducing and sulfur containing atmospheres, the vulnerable parts of the apparatus need special protection. For instance thermoelements are protected with stainless steel [12, 15], or placed outside the reaction chamber [17, 19]. In some cases the sample holders are constructed as baskets, made from platinum gauze, for better contact with the gasphase [13, 17, 19, 20]. A special instrument is the tubular

reactor/TG combination, constructed by Hakvoort [18, 19]. Within this instrument sorbent reactions are investigated at increased pressure (up to 10 bar) and at high gas flow rate (up to 2 m/s), with a maximum temperature of 1000°C. In this way the conditions in pressurized fluidized bed combustion can be imitated. Also the contact between gas phase and sorbent is optimized, because the gases are flowing through the column of sorbent (see Fig. 1).

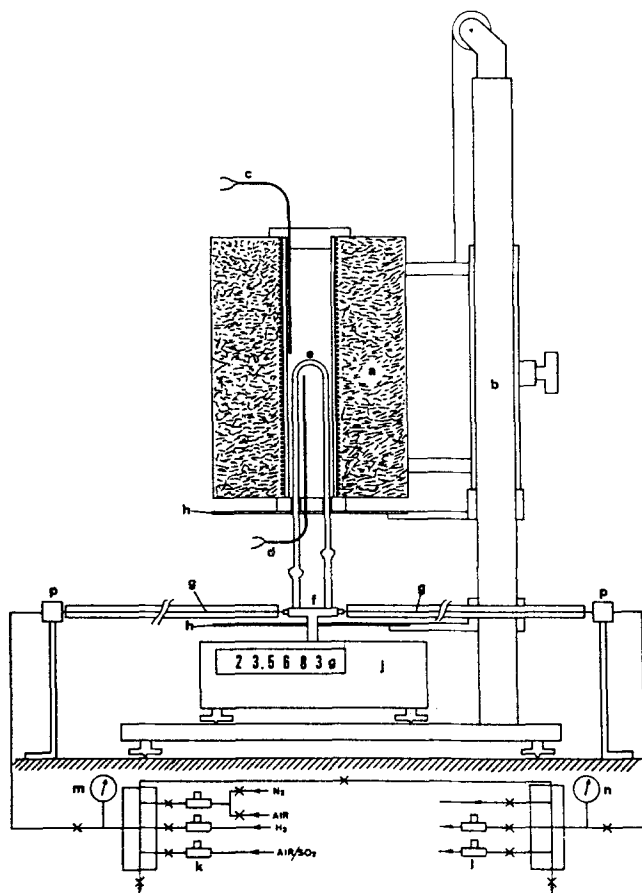


Fig. 1 Tubular reactor/TG combination a: furnace, c: and d: thermocouples, e: flowthrough tubular reactor, made of quartzglass, g: capillaries for gas in- and outle, j: balance for continuous weight registration

B. Rate of sulfur release during coal combustion, measured with TG and EGA. According to Schouten *e. a.* [9, 10] the sulfur in coal is present as pyritic, organic or sulfatic sulfur. The organic sulfur comes free together with

the combustion of the connected coal matrix (volatiles and char) while the pyritic sulfur shows several distinct sulfur release peaks. The decomposition of the sulfatic sulfur, mostly CaSO_4 , not always proceeds: only by reaction with SiO_2 from the ash, or at very high combustion temperatures.

C. Proximate analysis of coal with TG, using a variable atmosphere [8, 23]. Heating in N_2 to high temperature, followed by combustion in O_2 gives the contents of water, volatiles, fixed carbon and solid residue.

An elaborate example of this kind of analysis is given by Mikhail and Turcotte [22]. They analyse the solid reaction products of FBC of coal, together with limestone for sulfur uptake. This residue contains H_2O , $\text{Ca}(\text{OH})_2$, CaCO_3 , Carbon, Fe_2O_3 and CaSO_4 , and a mineral fraction. Analysis is performed with the following program:

Heating in N_2 from 20–750°C gives successively H_2O , $\text{Ca}(\text{OH})_2$ and CaCO_3 .

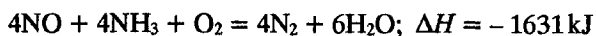
Reaction with O_2 at 750°C gives the carbon content.

Reaction with N_2/H_2 at 550°C gives Fe_2O_3 .

Heating in N_2/H_2 from 550–875°C gives CaSO_4 .

The (non reacting) mineral fraction can be calculated.

D. Removal of NO_x in exhaust gases by catalytic reactions with NH_3 . Biermann, *c. s.* [4, 5] developed a special catalyst, V_2O_5 on $\text{SiO}_2/\text{TiO}_2$, for the selective catalytic reduction of NO_x in exhaust gases, according to the exothermic reaction:



Investigations are made with a coupled DSC/MS combination in the temperature region 150–400°C.

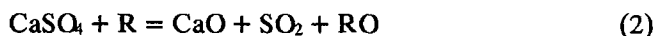
E. Sulfur capture and regeneration of sorbents.

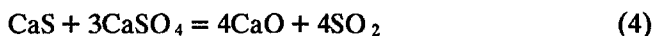
Both processes, capture and regeneration, are investigated by many investigators, using TG apparatus [6, 7, 11–21]. Important reactions are [6, 17, 20, 21].

Uptake of sulfur:



reduction:





The equilibrium SO_2 pressure can be calculated with Eq. (4), being a combination of (2) and (3).

This SO_2 pressure is 0.05 atm at 950°C , 0.1 atm at 1000°C and 0.5 atm and 1100°C [24]. This means that production of SO_2 at high concentrations needs high regeneration temperatures, much higher than usual in FBC.

This can be solved by the use of a second oxide (Al_2O_3 , SiO_2 or TiO_2) that stabilizes the CaO in Eqs (1) and (2), giving a different reaction mechanism according to

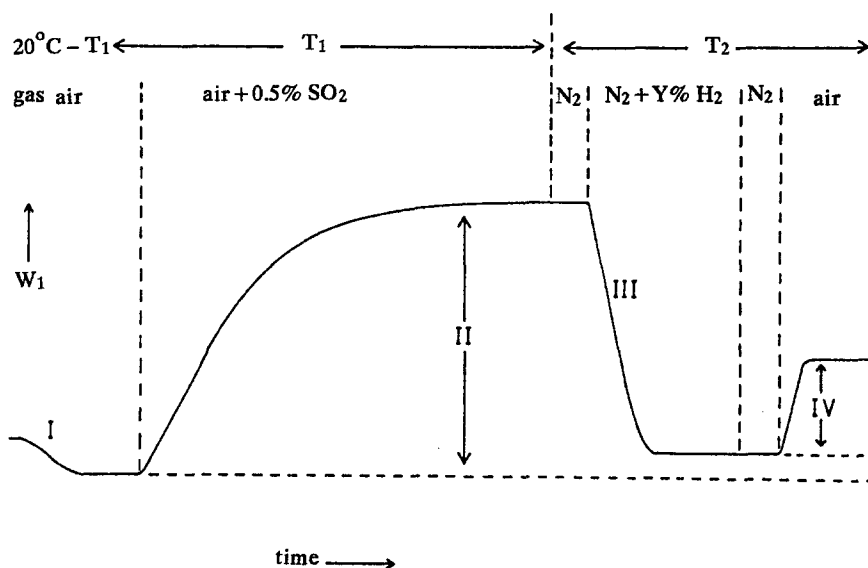
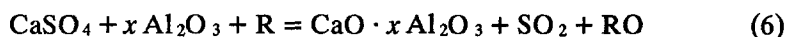
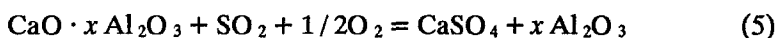


Fig. 2 SRO test, measured with TG: I Calcination, II Sulfation ($\text{CaO} \rightarrow \text{CaSO}_4$), III Regeneration ($\text{CaSO}_4 \rightarrow \text{CaO} + \text{CaS}$), IV Oxidation ($\text{CaS} \rightarrow \text{CaSO}_4$)

Stabilization of the CaO (giving $\text{CaO} \cdot x \text{Al}_2\text{O}_3$) shifts the equilibrium (4) or (8) to the right, resulting into higher SO_2 pressures.

A good TG test for sulfation, regeneration and cyclic behaviour of sorbents is the so called SRO test (Sulfation, Reduction and Oxidation), described by Hakvoort and Duisterwinkel [17, 21] (see Fig. 2). With this test the sulfation rate and sorbent capacity are determined during the sulfation, while the CaO/CaS proportion, formed during the regeneration can be calculated by measuring the oxidation reaction of CaS:



Many different sorbents are investigated for sulfur capture and regeneration: for instance:

- a. limestone, dolomite or oil shale [11, 13, 14, 16, 17]
- b. aluminates, CaAl_2O_4 , BaAl_2O_4 [12, 15]
- c. titanates, BaTiO_3 , CaTiO_3 [12, 15, 17, 21]
- d. calcium aluminate cement, CAC [12, 15, 21]
- e. composites: CaO on $\alpha\text{-Al}_2\text{O}_3$ [17, 18, 19, 21]
 CaO on $\gamma\text{-Al}_2\text{O}_3$ [18, 21]
 sol-gel pellets, consisting of a monolayer of CaO on Al_2O_3 [18, 20, 21]

The following properties are found:

– Complete sulfation is only possible with composites, consisting of a porous carrier material (Al_2O_3) and a relatively thin layer of CaO on the surface. The other compounds (group a–d) are not completely sulfated because the produced CaSO_4 forms a gastight layer around the sorbent particles.

– When the aluminates, titanates and CAC are regenerated at low temperature, a large amount of CaS is formed. This indicates a poor chemical interaction between the CaSO_4 and the Al_2O_3 or TiO_2 .

– Only the composites show a good regeneration behaviour at low temperature (850°C). Particularly the sol-gel pellets behave very well in long term cyclic experiments at low temperature.

Conclusions

– Thermal analysis, and particularly TG, is a good technique for investigation of the environmental problems, caused by coal combustion.

- Variable atmosphere TG can be applied for analysis of the composition of coal and solid residue.
- The capacity of sulfur uptake, the regeneration and the cyclic behaviour of sorbents can be investigated very well with (specially designed) TG.
- A combined TG/MS apparatus can be used for measuring the efficiency of sulfur removal from combustion gases.
- Catalysts for the selective catalytic reduction of NO_x by NH_3 can be investigated with DSC/MS.
- Realistic reaction conditions for atmospheric or pressurized fluid bed combustion of coal can be simulated in a tubular reactor/TG combination.
- One has to keep in mind that the experimental conditions, like contact between solids and gas-phase and superficial gas velocity, in most cases are very different for thermal analysis experiments and fixed bed or fluidized bed reactor measurements.
- More research is necessary for finding inexpensive sulfur capture sorbents, suitable for low temperature regeneration.
- Also more study is needed in order to prevent the NO_x production during coal combustion, or to remove the NO_x out of the exhaust gases.

References

- 1 G. R. Davis, *Scientific American*, 263 (1990) 21.
- 2 W. Fulkerson, R. J. Judkins and M. K. Sanghvi, *Scientific American*, 263 (1990) 83.
- 3 I. W. Noordergraaf, P. J. van den Berg, *PT/Procestechneek*, 38 (1983) 15.
- 4 J. J. P. Biermann, H. den Daas and F. J. J. G. Janssen, *Thermochim. Acta*, 133 (1988) 169.
- 5 J. J. P. Biermann, *The Behaviour of Ammonia in the Selective Catalytic Reduction of Nitrogen Oxide and in the Selective Oxidation by Oxygen*. Thesis, Enschede 1990, ISBN 90-353-1025-x.
- 6 A. Duisterwinkel, *Clean Coal Combustion with In Situ Impregnated Sol-Gel Sorbent*, Thesis, Delft 1991, D.U.P. Delft.
- 7 E. H. P. Wolff, *Regenerative Sulfur Capture in Fluidized Bed Combustion of Coal: a Fixed Bed Sorption Study*, Thesis, Delft 1991, D.U.P. Delft.
- 8 S. St. J. Warne, *Thermochim. Acta*, 166 (1990) 343.
- 9 J. C. Schouten, G. Hakvoort, P. J. M. Valkenburg and C. M. van der Bleek, *Thermochim. Acta*, 114 (1987) 171.
- 10 J. C. Schouten, F. Y. Blommaert, G. Hakvoort and C. M. van der Bleek, *A Thermal Analytical Study on the release of sulfur during coal combustion*, in: *Coal Science and Technology 11*; J. A. Moulijn, K. A. Nater and H. A. G. Chermin (Eds.), Elsevier, Amsterdam 1987, p. 837.
- 11 L. H. Fuchs, E. L. Nielsen and B. R. Hubble, *Thermochim. Acta*, 26 (1978) 229.
- 12 L. A. Ruth and G. M. Varga, Jr., *Thermochim. Acta*, 26 (1978) 241.
- 13 R. Snyder, W. I. Wilson and I. Johnson, *Thermochim. Acta*, 26 (1987) 257.
- 14 N. H. Ulerich, E. P. O'Neill and D. L. Keairns, *Thermochim. Acta*, 26 (1978) 269.

- 15 L. A. Ruth and G. M. Varga, Jr., *Env. Sci. Techn.*, 13 (1979) 715.
- 16 Ming-Shing Shen, J. M. Chen and M. Steinberg, *Thermochim. Acta*, 37 (1980) 247.
- 17 G. Hakvoort, C. M. van den Bleek, J. C. Schouten and P. J. J. M. Valkenburg, *Thermochim. Acta*, 114 (1987) 103.
- 18 G. Hakvoort, G. J. J. Overbeek, A. E. Duisterwinkel and E. H. P. Wolff, *Thermochim. Acta*, 135 (1988) 139.
- 19 G. Hakvoort and J. H. F. Grondel, *Thermochim. Acta*, 152 (1989) 105.
- 20 A. E. Duisterwinkel and G. Hakvoort, *Bull. Soc. Chim. Belg.*, 98 (1989) 439.
- 21 A. E. Duisterwinkel, E. B. M. Doesburg and G. Hakvoort, *Thermochim. Acta*, 141 (1989) 51.
- 22 S. A. Mikhail and A. M. Turcotte, *Thermochim. Acta*, 166 (1990) 357.
- 23 Du Pont Thermal Analysis Technical Literature, Application Brief TA-54.
- 24 J. M. Chen and R. T. Yang, *Ind. Eng. Chem. Fundam.*, 18 (1979) 134.

Zusammenfassung — Es wird zuerst eine Einführung über die Umwelteinflüsse auf die Kohleverbrennung gegeben. Dann folgt ein Überblick über die thermoanalytische Forschung auf diesem Gebiet. Moderne Themen sind dabei die katalytische Reduktion von NO_x in Auspuffgasen und die Entwicklung von Schwefel-Sorptionsmitteln zur Verwendung bei der Fließbett-Kohleverbrennung.