

## Coal and environment: Analytical aspects

Wolfgang Riepe

DMT-Institut für Chemische Umwelttechnologie Franz-Fischer-Weg 61, 4300  
Essen 13 F.R.G.

### **Abstract**

The structure and use of coal is reviewed. The importance of analytical methods to measure the major, and trace minor elements in coal and its products — ash, gases and environmental emission material, is stressed. It is shown how careful analytical control may diminish the emission of dangerous elements, hydrocarbons, sulphur and nitrogen oxides.

The mining and utilization of coal may cause environmental impacts in different ways. The influence of power generation liquification, gasification deposition of material and dumping of coal were investigated by analytical methods. See Figure 1.

Mining of coal may cause mining damage and subsidences, which consequently result in alterations of the surface including buildings.

Another direct effect of mining causes alteration of the landscape, either by deposition of wash tailings, by creating clearing ponds or by water utilization in general.

Now to coal itself! Coal is an organic rock, consisting of two essential parts: the organic and inorganic matter.

The components, bound with these parts, may affect the environment in a typical manner during coal utilization.

According to the particular process of conversion different products with different quantities are formed.

The second part of coal is the mineral matter or after the corresponding conversion of coal termed ash or slag, which may be used to a major part as commercial products. The major part of trace elements present in coal is bound to the mineral matter, especially to the sulphitic components. Care has to be taken that these trace elements do not get released to the environment in an uncontrolled fashion.

Until now influences have been delineated, which are introduced directly by the coal into the corresponding processes of utilization and laborization. Many other products, which affect the environment, are formed during the conversion itself. During the combustion processes, essentially used for the production of electricity and heat, certainly  $\text{CO}_2$  as a climate influencing emission is produced, but also  $\text{SO}_2$  and  $\text{NOX}$  as well as the special component  $\text{N}_2\text{O}$  are relevant products affecting the environment. With unfavourable conditions even toxic compounds may be formed, of which dioxin may be cited here as but one.

Environmental Influence

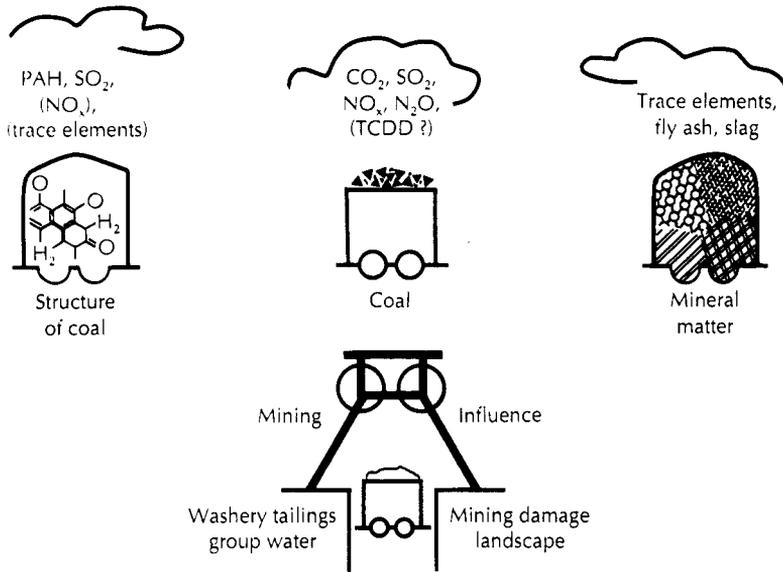


FIGURE 1

The task of coal analysts consists essentially in creating the fundamental knowledge for the development and optimization of technical processes, to avoid or to reduce environmental problems. See Figure 2. The main product formed by coal combustion for heat and electricity production because of its quantity is CO<sub>2</sub>. Three tons of CO<sub>2</sub> result from one ton of hard coal, that is 1.500 m<sup>3</sup> of CO<sub>2</sub>. It is highly unlikely that a CO<sub>2</sub>-free combustion of coal will ever be invented. Therefore, emphasis has to be set on strategies of avoidance, i.e. the more economical use of energy resources, but also the increase of efficiency, which is on the other hand a challenge to engineering. By gas and steam-processes, degrees of efficiency of more than 50 % seem possible.

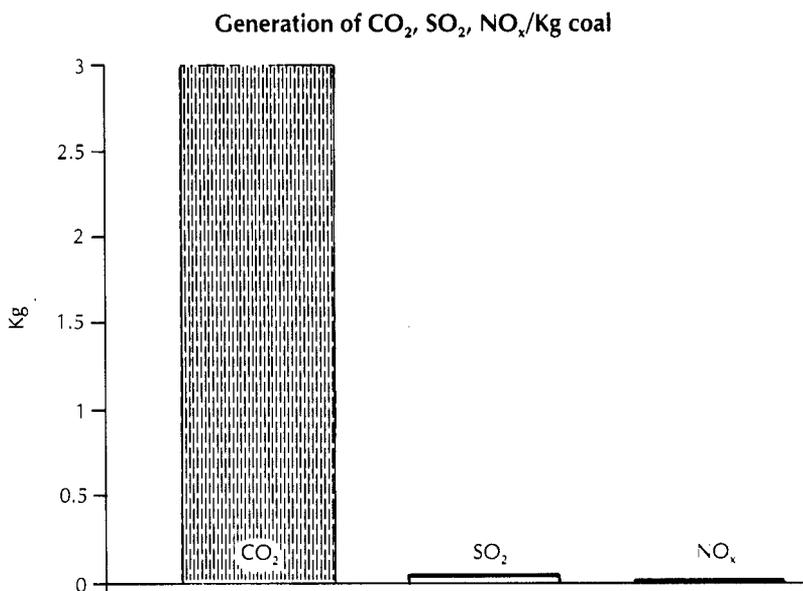


FIGURE 2

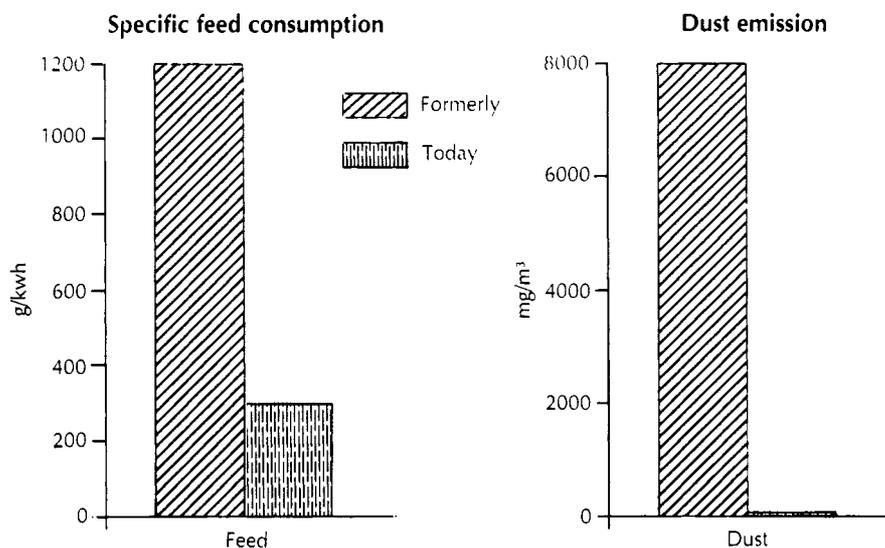


FIGURE 3

Figure 3 shows, that the specific coal consumption has been reduced from 1200 g/kwh to 300 g/kwh today by technical progress. Therefore, by more efficient precipitation, dust emission has diminished from 8000 mg/m<sup>3</sup> to 50 mg/m<sup>3</sup> flue-gas. At the same time emission bound to particles, especially toxic or near toxic trace elements, has decreased accordingly.

This fact is related to the condensation of compounds vaporized in the combustion chamber and settling predominantly onto the finer grained particles of the fly ash (Figure 4) when the flue gases are getting cooler. These elements are therefore strongly enriched in the fine grain size fraction (< 10 μm). PAH-compounds are deposited in a similar manner. The enrichment within the fine grain size fraction is evident also by a comparison of the element concentrations found in the entire filter ash with those of the ash from the last stage of the precipitator. Distribution factors may be derived thereof, which describe the relation of concentrations and enable a qualitative statement about the extent of vaporization and condensation within and at the end of the firing installation.

Elements with a low distribution factor (1–2) are volatile only to a low extent even under the conditions in the combustion chamber. Elements with a higher distribution factor (>2) are vaporized in the combustion chamber to a large extent and condense almost entirely, so that they are present in the fine particles of the fly ash and hence also within the emission of clean gas dust.

Figure 4 gives distribution factors derived from the entire filter ash and the ash of the fifth stage of the filter for some elements. In this presentation it is assumed, that 10% of the whole ash of the coal leaves the power station as coarse ash, 90% as filter ash and less than 0,1% through the chimney stack. Graphic presentation in Figure 5 about the recovery ratios of diverse elements shows, that apart from mercury, selenium and perhaps also arsenic all elements investigated are bound to the filter ash almost to 100%. On the basis of this balance a significant volatile part of the cited elements cannot be determined. On the other hand the volatility of the elements mercury and selenium is wellknown. It is to be expected that mercury, selenium and partly arsenic within the flue gas ahead of the desulphurisation stage are present in the gas phase. An investigation of the entry of heavy metals into the flue gas desulphurisation process, therefore may not be restricted to an investigation of the clean gas dust, i.e. the solid particles, but has to be extended also to the gaseous compounds.

Because of the mass entering the atmosphere, the next strongest influence on environment results from SO<sub>2</sub> and NO<sub>x</sub>.

		E-Filter dust (total)	E-Filter dust (5-stage)	Distribution factor
As	mg/kg	55	160	2.9
Be	mg/kg	20	31	1.6
Bi	mg/kg	2	10	5.0
Cd	mg/kg	2	7.6	3.8
Co	mg/kg	183	249	1.4
Cr	mg/kg	274	248	0.9
Cu	mg/kg	321	652	2.0
Hg	mg/kg	0.59	0.19	0.3
Ni	mg/kg	465	600	1.3
Pb	mg/kg	267	754	2.8
Sb	mg/kg	25	89	3.6
Se	mg/kg	5.3	35.1	6.6
Te	mg/kg	<0.5	1.6	>3.0
Tl	mg/kg	5.1	12.8	2.5
V	mg/kg	529	862	1.6
U	mg/kg	11	23	2.1
Zn	mg/kg	359	1.200	3.3

Distribution factors of filter ashes

FIGURE 4

By upgrading activities it is possible to separate and collect the inorganic sulphur vastly. But until today no technical process is known, which allows to a larger extent the elimination of organic sulphur from coal. It is supposed, that about 50% of the organic sulphur is contained in the coal molecule in the form of dibenzothiophene or similar compounds. Moreover linkages of aromates by sulphur-bridges also have been detected by corresponding investigation.

There are assertions in the scientific coal literature, that organic sulphur may be eliminated for example microbiologically or by chemical treatment.

To activate microorganisms aimed at the decomposition of organic sulphur compounds, it is firstly necessary to develop analytical methods which allow the determination of the chemical bonding form, respectively the composition of the sulphur containing organic molecules. A starting point for obtaining this information about sulphur may be by using solid state NMR-spectroscopy with a MAS-technique. Hitherto this has not been successful because of low sensitivity, i.e. the weak magnetic moment or the gyromagnetic ratio of sulphur respectively and its relatively low number of isotopes.

Another starting point may be mass spectrometry, where coal is vaporized by high temperatures in the vacuum of the ion source chamber and ionized there by an electron impact or otherwise by chemical ionization. A special technique, the so-called evaluation of homologous Z-series, can be used for this, which enables certain information to be obtained.

The situation for nitrogen is similar to sulphur. Apart from  $\text{NO}_x$  which is formed during combustion with nitrogen from the air and which may be reduced by appropriate combustion techniques, there is still a part of fuel nitrogen, which also cannot be eliminated economically from the coal within a reasonable space of time. Of course there are also proposals here and trials for its elimination on condition that information about the chemical structure of the nitrogen components is available.

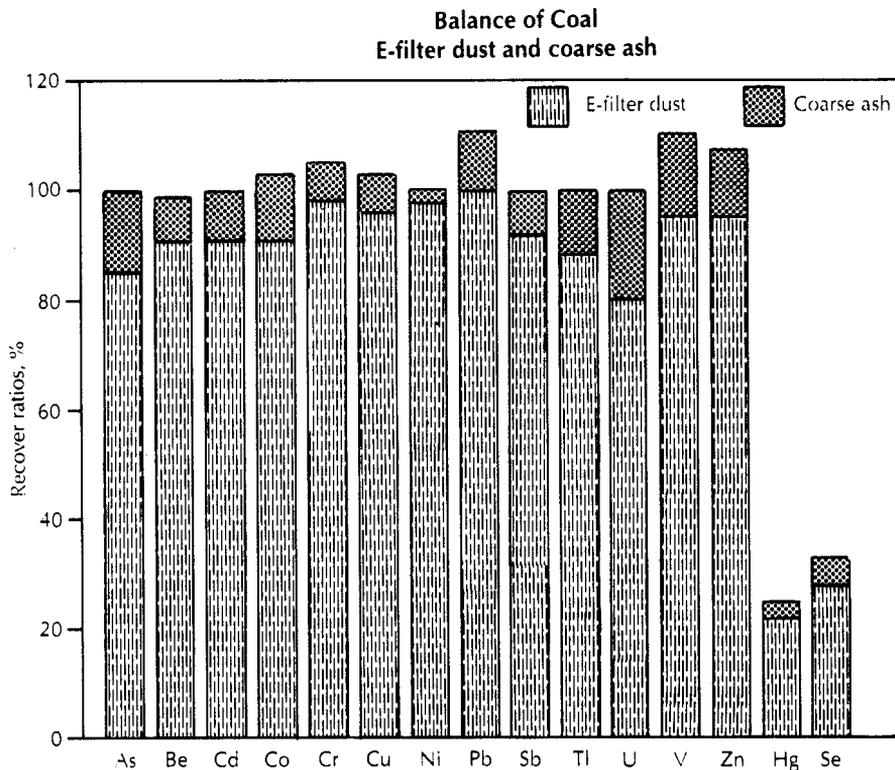


FIGURE 5

As has been explained before, the emission of trace elements, with the exception of mercury and occasionally selenium and arsenic, is no longer a problem in the field of power and heat generation since the introduction of secondary techniques for the washing of flue-gases, because these elements are retained by the washing water, from which they are eliminated by an appropriate waste water cleaning process. The still remaining elements, mercury, arsenic and selenium are eliminated by an additional adsorption stage, for example with activated coke.

For the elimination of wastes from power plants there is only a partial need of further investigations. The major problem is the reuse commercially. In the case of critical residues their environmental behaviour has to be tested and if necessary, the potential of danger has to be abolished by leaching and/or thermal inertization.

Testing procedures similar to practice are necessary therefore to discern environmental impact. In the following, considerations and solutions for the investigation of the leaching behaviour of power station wastes are presented.

Two major errors can be made with the disposal of material of which the leaching behaviour is unknown. Taking into account the enormous quantities of these substances which can be produced, the ecological and economical consequences of both mistakes can be significant.

- The disposal of ecologically harmful material without suitable precautions may lead to severe ecological damage.
- The disposal of ecological harmless material on a special waste dump leads to financial losses which may possibly cause considerable economic problems. Above all, however, special waste dump sites are rare and therefore should not be used unnecessarily, because this would, in the end, cause ecological damage too, by making these areas unusable for other purposes.

This shows that with insufficient knowledge of the leaching behaviour of these materials, it can be just as dangerous to play it always safe as to be careless and irresponsible. Consequently, the exact knowledge of the leaching behaviour is essential for the - intermediate or final disposal of such mass products.

In the Federal Republic of Germany, the test most commonly used for the evaluation of leaching behaviour is the shake test in compliance with DIN 38 414 S4. The sample material — usually 100 g — is shaken carefully for 24 hours in a leaching medium (10 times the mass of the dry matter) so that the particles are not crushed. The filtered leachates are analyzed and the data obtained are then compared with the threshold values given in guidelines or guideline drafts (1 to 3). With this leaching method, the only liquid/solid ratio used is  $Q = 10$ .

The cascade shake test (Figure 6) is based on the simple shake test just described with  $Q = 10$ . This test is continued by dividing it into two subtests. In the first one, solid matter which has already been leached out is mixed with fresh water and is leached out furthermore. The liquid/solid ratio is thus growing continuously. In the second subtest the filtrate, which has already extracted substances from the sample, is mixed with new solid matter so that more soluble substances can be leached out. In this subtest, the values diminish steadily. In the cascade shake test, the  $Q$ -values can be varied in a large range from less than 1 up to some 100's in short intervals of time. This is to determine the maximum leachable quantity of the different components (with large  $Q$  values) and the largest possible concentration of various components in the leachate respectively (with smaller  $Q$  values).

The comparison of these lab tests with the processes taking place on a real dump shows that there are considerable differences. The shake tests, for example, do neither consider the permeability of the material nor mineralogical-chemical and microbial effects. The influence of the alternation of rainy and dry periods, which is probably of great importance in reality, is also not taken into account. These difficulties are already mentioned in the text of DIN 38 414 S4: 'This test method (DIN 38 414 S4) may, however, bring about measuring values which will only be reached in the long term, if ever, on a real dump. The harmfulness of a material disposed or to be disposed must not be determined from the analytical values alone.' The text continues: 'Consequently, the leaching behaviour of individual substances, which is quite a complex analytical problem, can only be assessed by an expert.'

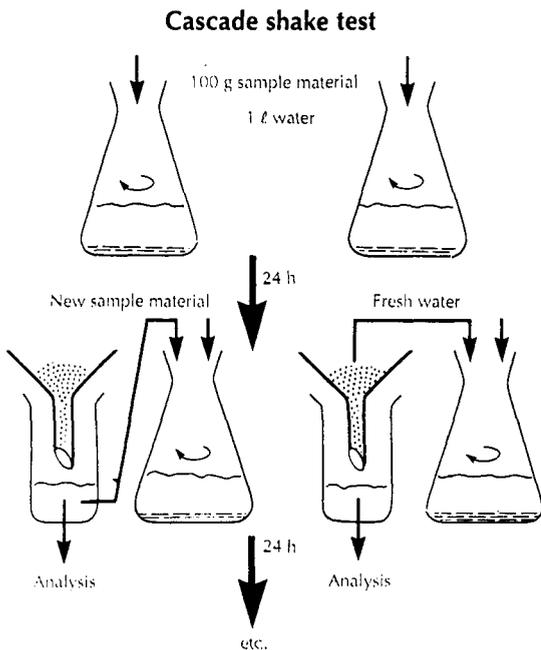


FIGURE 6

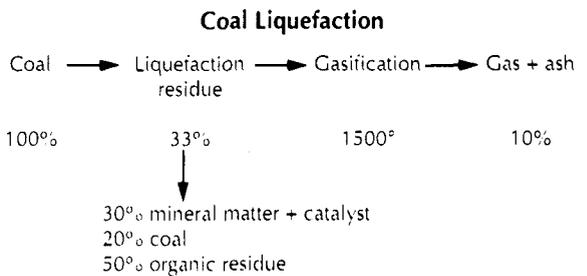


FIGURE 7

With laboratory column-leaching, where generally an excess amount of water is used, long-term effects and the alternation of rainy and dry weather are also not taken into account.

### **PRACTICE-ORIENTATED LARGE SCALE LYSIMETERS**

In the Bergbau-Forschung GmbH, the predecessor of the DMT-Gesellschaft für Forschung und Prüfung mbH, large-scale lysimeters have been developed and used, which permit the simulation of the leaching process under real dump conditions but are nevertheless more variable and easier to handle than 'lysimeter dumps' (dumps designed to function like a lysimeter) or test dumps.

The lysimeters are only eluted by natural rainfall and are not irrigated artificially. Consequently, they are exposed to the same alternation of rainy and dry periods and to the same dilution and concentration processes due to intermediate evaporation as a real deposit. The effluents from the peripheral area and from the central area are each collected at the bottom of the lysimeter via a siphon trap. This is to prevent atmospheric oxygen from getting into the lysimeter, because this might influence microbial reaction. Another environmental influence by coal directly is caused by middle and long term storing. The same effects outlined for power station byproducts and additional atmospheric and microbial reaction as oxidation for example of pyrite may cause a cascade of secondary processes.

We have studied such processes in a temperature controlled lysimeter under inert and atmospheric conditions (oxidation, rainy periods). The coals we have obtained are varied in coal rank, ash content, grain size distribution, pyrite content and pyrite distribution. The effluents were analyzed for organic and inorganic parameters. During a period of 2 years no significant mobilization of organic and inorganic substances was obtained.

The decreasing of the pH-value may have been caused by different factors. First, oxidation of pyrite by microbial activities (*thiobacillus ferrooxidans*) produce sulphide acid. These effects depends on pyrite content, pyrite distribution (syngeneic or epigenetic) and grain size of the coal. In the case of buffer capacity by  $\text{CaCO}_3$ , the pH-value may be stabilized till exhaustion of  $\text{CaCO}_3$ . Decreasing of the pH causes mobilization of metals such as As, Pb, Cd etc. which are included in the sulphitic matrix.

All these effects require additional protection steps to avoid environmental impacts.

Considering now the valorization processes, during gasification and liquefaction with regard to their environmental impact it is necessary to ascertain what may really affect the environment during sluicing of the material streams, especially of the residues. This may also be caused by flue dust in the raw gas, by the raw gas itself and by the process water. The same elements as found with combustion processes are found here and the techniques of diminution are here essentially the same as with the combustion processes. Another problem may be seen therein, viz, that these residues cannot be deposited in an environment protective manner without effects especially in the case of alkaline catalysts. A solution could be, to introduce a stage of inertization before deposition. For example, this may be a thermal treatment. The investigations required are the same as for power station byproducts.

In the case of coal liquefaction, in particular in the process of liquid-phase-hydrogenation, injuries of the environment may be minimized and easily controlled because of the closed system. The formation of phenols in former times and the environmental problems caused thereby may be avoided by appropriate operating conditions. The compounds  $\text{H}_2\text{S}$  and  $\text{NH}_3$  contained in process water and gas may be eliminated without any problems. There remains only to eliminate the mineral residue of the hydrogenation process in an environment protecting manner. Here the same procedure may be followed as has been suggested for the gasification residues. Figure 7 shows that by combination of liquefaction and following with the gasification of the liquification residues at 1.500 °C, no more than about 10 % ash is produced which is inert and ready for deposition.