

## **Demineralization and Desulfurization Process to Generate Clean Coal**

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Aim of this work was the development of processes to obtain clean coal. To this end samples of different coals were leached with acidic and/or alkali solutions, under different conditions of pH, temperature and time for each treatment. Generally, HF aqueous solution treatment drastically reduced mineral matter of samples, but it had no effects on sulfur content. Further treatments, carried out with different solvents gave promising results for sulfur removal. After each treatment, coals were subjected to thermogravimetric analysis (TGA) coupled with mass spectroscopy (MS) of gases formed during combustion. TGA yielded samples ash content and, indirectly, the mineral matter content while MS provided samples sulfur amount.

### **1. Introduction**

Some disadvantages of the use of coal as fuel with respect to gas and liquid fossil fuels are due to slagging and fouling in the combustion chamber, and to the emissions of toxic particulate matter, trace metals and SO<sub>2</sub>. All this represents an important concern in the design and operation of pulverized coal fired boilers since it determines the size and the cost of the boiler and of the desulphurization and deashing plants downstream the boiler. These problems could be overcome if the coal were pretreated to remove mineral matter to obtain a clean coal.

Nowadays, there is not a technically and commercially suitable technology for clean coal production. However, there are a number of relevant patents related with this topic (Kinding and Reynolds, 1987; Reggel et al., 1976; Waugh and Bowling, 1987; Yang, 1979; Lloyd and Turner, 1986). In addition, some studies, aiming at investigating peculiar aspects of the process, were published (Steel et al., 2001; Benson and Holm, 1985; Ciambelli et al., 2003; Chen and Zhang, 1999; Davidsson et al., 2002; Baláz et al., 2001). In such studies acid solutions as well as basic solutions were employed (Davidsson et al., 2002; et al., 2001). The importance of grinding associated with leaching was also pointed out (Baláz et al., 2001). In any event, the main objective of such works was to expand the knowledge of the key aspects in order to contribute to the realization of suitable processes for coal demineralization.

The objective of this work was to explore the possibility to set up a coal demineralization process for the production of clean coal to be used for combustion.

This was accomplished by performing physical and chemical treatments of two coals and analyzing their characteristics before and after the treatments.

## 2. Experimental

### 2.1 Materials

Four sub-bituminous coals have been employed in this study: an high volatile colombian coal, El cerejon (EC), a medium volatile coal, Kleinkopje (KLK) and other two coals characterized by high mineral content, i.e. Medupi (ME) and Kusile (KU). The latter two have been chosen because their high mineral content makes them particularly suitable for the treatment object of our study even though their sulfur content is comparable to that of the other two coals. Their proximate and ultimate analyses are reported in Table 1. Data shows that they have similar carbon content and, therefore, a comparable ageing degree although EC coal is richer of volatiles.

Table1 Proximate and ultimate analyses of coals

	EC	KLK	ME	KU
<i>Proximate analysis dry basis (wt %)</i>				
Volatiles	36.4	24.4	25.5	23.0
Fixed carbon	53.5	60.2	42.8	39.3
Ash	10.7	15.4	31.7	37.7
<i>Ultimate analysis dry basis (wt %)</i>				
S tot.	0.8	0.5	1.3	0.6
C	72.1	74.1	55.4	49.2
H	4.5	3.8	3.5	2.5
N	1.3	1.6	1.2	1.1

### 2.2 Equipment and techniques

The experimental procedure to realize the selective demineralization is that already set up by the author and reported in a previous study (Cirillo et al., 2009). Coals were first ground in size below 38  $\mu\text{m}$  then subjected to the selective demineralization process, which, as reported in Fig. 1, included several steps in cascade. Each step comprised the mixing of the solid sample with an extracting solution for a given time at a given temperature, then the filtration of the solid residue, its washing with distilled water until the exhaust water does result almost neutral and, its drying. The solution obtained after each step was analyzed for the content of metal ions by plasma atomic emission spectrophotometry (ICP-AES) of dissolved samples using a Varian Liberty II. The solid residue was partly used for combustion tests and partly for further demineralization processes. Combustion tests were performed to assess the residual ash and, indirectly, the amount of removed minerals. Such tests were carried out by temperature-programmed thermogravimetric analysis (TGA) in air flow with a thermoanalyzer (TA instruments). Air flow rate was 50  $\text{Ncm}^3\text{min}^{-1}$  and the rate of temperature increase from 293 to 1250 K was 10  $\text{Kmin}^{-1}$ . To evaluate the amount of sulfur removed through the various treatments, mass spectrometry analysis (MSA) were carried out on the gas

coming from the TGA, with which it is possible to detect the type of gases generated during the combustion.

### 3. Results

#### 3.1 Demineralization

The residual ashes after samples combustion were analyzed by ICP OES and the results showed that most of the inorganic material present in the coals are silicates. In addition, the relative composition of the various oxides in the ashes of KU and ME coals are very similar, while significant differences there are between such two coals and KLK coal for what concerns calcium and manganese oxides.

In previous works the authors set up a process of selective demineralization based on the use in cascade of different solvents with increasing acidity (Ciambelli et al. 2003, Cirillo et al. 2009). The last step of such a process was coal treating with concentrated hydrofluoric acid (HF). In the present work the effect of the sole treatment with such a solvent was investigated because of the specific reactivity with silicates based minerals, which represent, as mentioned above, most of the inorganic material present in the coal. Therefore, tests were carried out treating coal by concentrated HF aqueous solutions (50 wt%). Further tests were performed decreasing the HF concentration in order to test the possibility to limit the amount of reactant used per unit mass of treated coal. Such tests were carried out at ambient temperature for one hour employing the same ratio between solution volume and coal mass.

*Table 2 Residual ash content of coals treated with HF solutions at various concentrations.*

HF Concentration (wt %)	TGA Residual mass ( wt %)			
	EC	KLK	ME	KU
50	0.7	0.57	2.2	4.3
25	0.88	1.12	6.24	8.85
10	2.27	2.7	5.78	11.9
0	9.7	14.4	29.7	35.3

Table 2 shows that the treatment with concentrated HF strongly reduces (from 96% for KLK to 87% for KU) the ash residual content of all the coal samples but also that the decrease of the HF concentration corresponds to an increase of the ash content in the TGA residue. Data in Table 2 corresponding to 0 wt % HF concentration are those of the untreated samples. Their values result slightly lower than those of the values of ash content of the samples reported in Table 1, because these latter are given on dry basis.

Further tests were carried out to assess, for given values of the other operating conditions, the influence of the HF mass/carbon mass ( $m_{\text{HF}}/m_{\text{coal}}$ ) ratio, an useful parameter for a possible industrial application of the demineralization treatment. Therefore, while the volume of the acid solution was progressively reduced, parameters such acid concentration (50 %), amount of coal (0.050 g), treatment time (one hour) and temperature (ambient) were kept constant. Results, in term of wt % of residual ash mass as a function of ( $m_{\text{HF}}/m_{\text{coal}}$ ), showed that the action of HF is still effective when the ratio ( $m_{\text{HF}}/m_{\text{coal}}$ ) decreases from 26.1 to 0.047 although at such a low value data are less

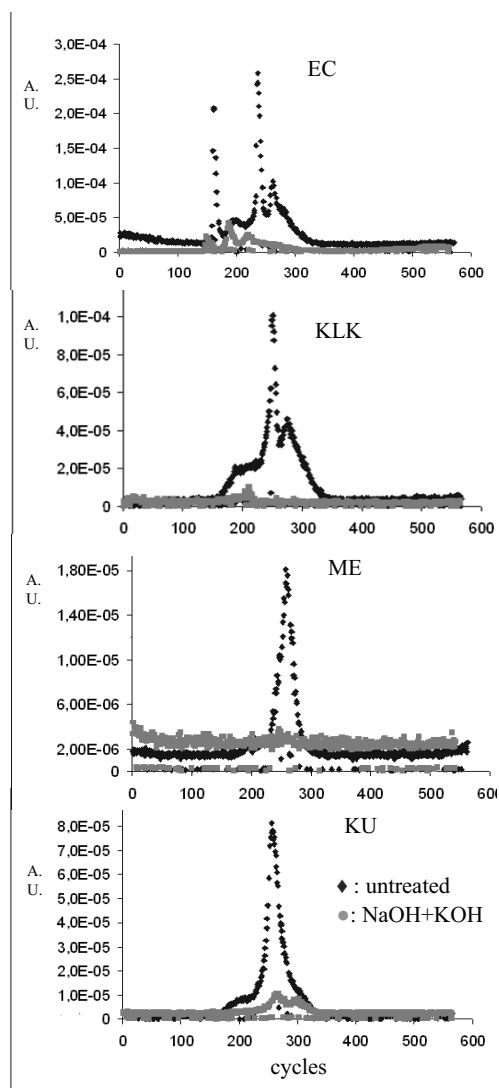


Figure 1 Sulfur related fragments emitted during the coal samples combustion. A.U.: arbitrary units

reliable because the amount of solution is just enough to wet the solid. A more reliable value of such a ratio is then 0.78. This parameter, however, changes when considering a coal sample much richer in ash as KU. Indeed, tests suggested that with this coal the value of the  $m_{HF}/m_{coal}$  ratio is markedly higher (about 10). If a correction is made, considering the different amount of minerals per unit mass of coals KU and EC, a value around 3 should be expected for the KU coal.

Further treatments were carried out to evaluate the minimum contact time between coal and solution to get a satisfactory demineralization. Results, not reported here, suggest that a contact time of 15 min appears to be enough. A further parameter investigated was the coal dust particle dimension. Since all the previous tests had been carried out with samples grounded below 38  $\mu m$ , new tests, employing EC and KLK coals, were performed with coal dust with dimensions below 250  $\mu m$ . Results clearly showed that the demineralization process appears unaffected by the coal dust dimension from 38 to 250  $\mu m$ . Such a results appears relevant in the view of an industrial application although other aspect of the combustion process could determine the value of such a parameter.

### 3.1 Desulfurization

The treatment with HF solutions had only negligible effects on the removal of sulfur, as evident from results of MSA carried out on the product gas of the combustion of coals

(not shown here). This is in agreement with literature findings where it is reported that pyrite is extracted only partially by concentrated HF (Finkelman, 1982).

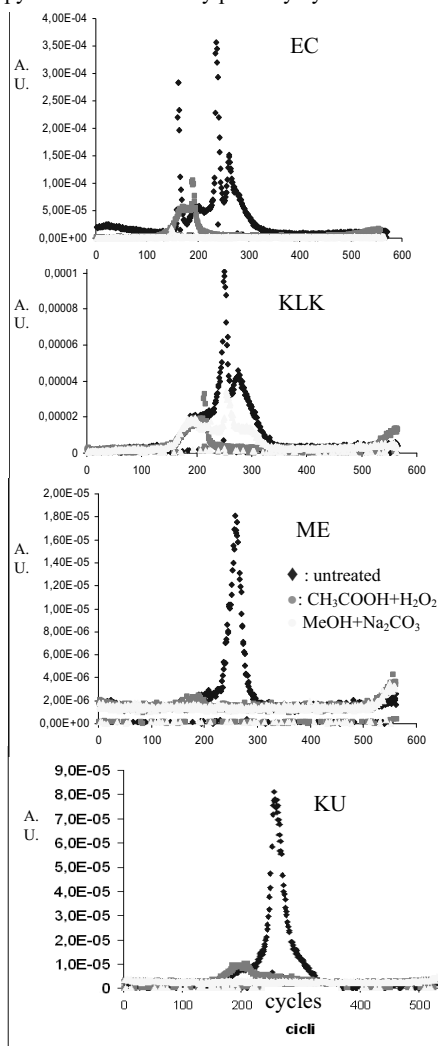


Figure 2. Sulfur related fragments emitted during the combustion of untreated and treated coal samples. A.U.: arbitrary units

yielding a residual ash content lower than that obtainable with the only treatment with HF 50 wt%. Instead, for what pertains to the desulfurizing effect, the combined treatment with  $\text{HNO}_3$  1.5 M and HF 10 wt % yielded the best results but it was effective only with EC coal leaving essentially unchanged the sulfur content of the other samples.

In this study to achieve sulfur removal, different treatments were carried out using acid or basic solutions alone or combined. One of these included a treatment with a 2 wt % NaOH and KOH (in the ratio 1:1) aqueous solution overnight at 60 °C, followed by acid treatments.

For all the samples the desulfurizing action of the basic treatment appears evident from the results presented in Figure 1, which reports the comparisons of MSA carried out on the product gas by the combustion of untreated and treated coals. Samples treated only with the basic solution showed an increase of the residual ash as percentage of the untreated sample mass while the same quantity, measured after basic treatment and HF concentrated treatment, was very similar to the values found after the sole treatment with HF solution.

Also the capability of an acid solvent ( $\text{HNO}_3$ ) for coal desulfurization was tested in this work because it can have a beneficial effect also on the demineralization of the coal. Its effect was tested when used alone or in combination with HF. It was employed alone at concentration of 1.5 M or in combination with HF 2 wt% or with HF 10 wt % or followed by the treatment with HF 2 wt% or with HF 10 wt %. From the mass of data pertaining to this investigation it can be resumed that for what concerns the demineralizing effect the treatment with  $\text{HNO}_3$  plus the treatment with HF 10 wt % attained the best demineralization

A further combined acid-base treatment was tested. It, realized under mild conditions, consisted of two steps. In the first, useful for the organic sulfur removal, the sample was treated with a mixture of acetic acid and  $H_2O_2$  for six hours at 50 °C. In the second, useful for removing inorganic sulphur, the sample was treated with a solution of  $Na_2CO_3$  in methanol. These treatments did not have effect on the residual ash content after combustion but they work very well in the removal of sulfur for all the coal samples tested in this work. This is shown in Figure 2, which reports the comparisons of MSA carried out on the product gas by the combustion of untreated and treated coals.

#### 4. Conclusions

Large amounts of silicon based minerals in the coal makes hydrofluoric acid the main solvent for coal demineralization. Results demonstrated that it has a strong demineralizing action even at relatively low ratios between acid mass and coal mass and at reduced contact times. The tested procedures for sulfur removal yielded satisfactory results: the best seems to be the combined treatment with acetic acid and  $H_2O_2$  followed by the treatment with the weak base.

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