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Kinetics of Sulcis Coal Chemical Cleaning Process

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Sulcis coal is a sub-bituminous coal from the Monte Sinni mine in the South West coast of Sardinia. The ash content of this coal is about 15 wt % as received, whereas the sulphur content is 6-7 wt% (inorganic sulphur is present at about 2-3 wt%). Since most of the pyritic sulphur is finely disseminated in crystals of micron or sub-micron size, the only remaining possibility of removing sulphur from this coal prior to its utilization is confined to chemical methods. The present work shows the results of the experimental testes which are conducted on Sulcis coal samples by sequential leaching of potassium hydroxide followed by hydrogen peroxide. Moreover, the present paper shows the kinetics of Sulcis coal leaching process. The high efficiency of sulphur reduction, on average about 30 %, was found to be of special technical relevance for relatively large particle sizes, <5.60 mm, said efficiency being obtained through tests carried out on different particle size classes of leached samples.

1. Introduction

Coal is a fossil fuel rich of elements different from carbon. A big amount of the coal reserves in the world consists of low rank and low quality coal, bearing high contents of ashes and sulphur. The significant environmental impact due to the high sulphur content of some coals, independently of ranking thereof, is one of the major limitations to their use in a thermoelectric power station. Sulphur can compose up to 12 % its mass but represents an undesired impurity as its combustion produces SO_2 gases which result in the formation of acid rain. Sulphur, contained as inorganic and organic compounds in the coal matrix, provides a serious drawback to the increased utilization of coal. Furthermore, future development of coal–oil, coal–water and coal–methanol fuel applications may require pre-combustion desulphurization to levels only achievable by chemical processing. It is might belief that it is technically feasible to remove sulphur from coal by different methods, but it is needed to evaluate the extra-cost of the treated coal. The cost of pre-combustion coal desulphurization is highly variable (Kawatra et al., 2001), depending on various parameter of the cleaning process. On average, coal cleaning adds 2-2 $/t (metric) to the cost of coal.

Pyritic sulphur and mineral matter are generally removed from coal through gravity concentration or froth-flotation processes, but these methods cannot remove organic sulphur, which in some cases reaches 50 % of the total, and requires to be processed through chemical desulphurisation methods, also effective in removing part of inorganic sulphur and mineral matter. Since most of the pyritic sulphur is finely disseminated in crystals of micron or sub-micron size, the only remaining possibility of removing sulphur from this coal prior to its utilization is confined to chemical methods (Carbini et al., 1990).

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Leaching is also called solid-liquid extraction; it is in fact a process which aims to separate soluble components from a solid mass by using a proper solvent. Leaching with chemicals may be carried out to reduce ash and sulphur concentration in coal. In coal industry, both biological and chemical leaching are used; the chemical one relies mainly on mineral acids, but efficaciously utilizes also some bases in the form of molten caustic mixtures, or combinations of these with oxidising reagents.

2. Experimental

Sulcis coal with particle size < 5.60 mm was treated with a two-stage leaching sequence of aqueous solution of KOH followed by aqueous solution of H_2O_2. The ultimate analysis of untreated Sulcis coal sample is presented in a previous paper (Fois et al., 2010). The Sulcis coal, classified as sub-bituminous, has a low heating value (as received) of 20.14 – 21.76 MJ/kg. This parameter was measured by using a high-pressure oxygen bomb calorimeter (LECO AC 500). Ash analysis was performed by using a Thermo Gravimetric Analyzer (TGA, MAC 400). In a previous paper (Fois et al., 2010) mineral matter of Sulcis coal was identified by X-ray diffraction analysis (XRD) and by X-ray fluorescence analysis (XRF). Moreover, Figure 1 shows the SEM (Scanning Electron Microscope) image of this coal. The SEM instrument used was a FEI Quanta 600 equipped with energy dispersive analysis by X-rays (EDAX), which allows the elements present to be identified.

Leaching tests were performed with a coal sample size of 20 g and a solution volume of 50 ml and carried out in a 250 mL agitated beaker. First step leaching experiments were carried out by using 1.78 M KOH solution at isothermal room conditions. However, second step leaching tests were conducted at different temperatures (T = 15 °C , 25 °C, 30 °C and 40 °C) and at 20 % volume of H_2O_2, in presence of 0.2 M H_2SO_4. The temperatures were maintained by using a water bath and the treatment time for these reactions were investigated. After the end of each reaction step, the leached samples were recovered by filtration, dried at 90 °C and analyzed for weight and total sulphur content. This parameter was determined by using a sulphur analyzer (SC132). In fact, high temperature combustion methods (ASTM D4239), the coal is first burned in a tube furnace at 1350 °C or higher in a stream oxygen, to convert the sulphur completely into gaseous oxides. Pyritic sulphur was determined by measuring the quantity of pyritic iron present, while pyrite does not dissolve in hydrochloric acid, but does dissolve in nitric acid (ASTM D2492). Furthermore, sulfate sulphur is mainly from oxidation of pyrite and consists of iron sulfates, which are soluble in hydrochloric acid (ASTM D2492).

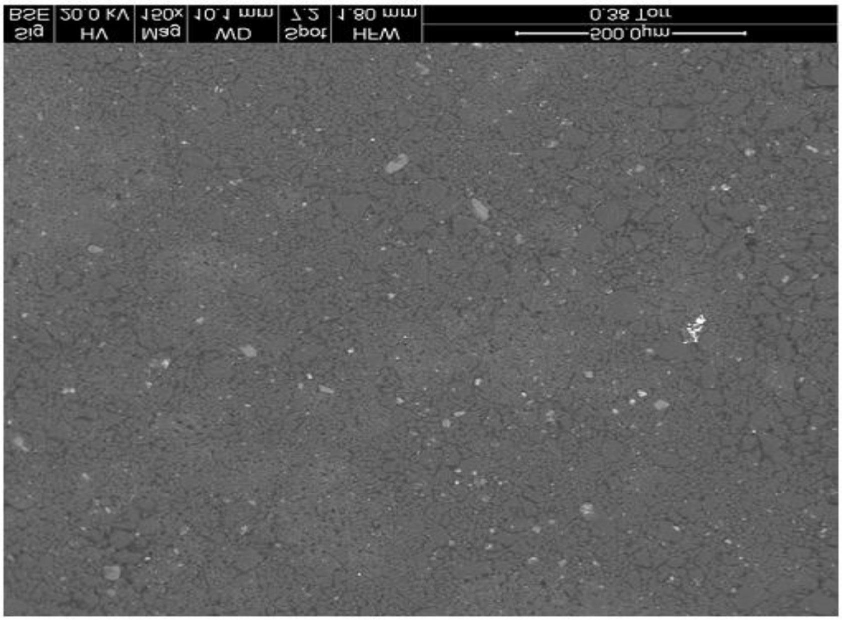

Figure 1 SEM image of Sulcis coal

3. Results and discussion

The experimental results concerning this paper are put in Table 1 and Table 2, for first and second leaching step, respectively. Then, the experimental degree of total sulphur conversion after each leaching step was calculated by using the following equation:

$$X = 1 - \eta \frac{S}{S_0} \tag{1}$$

which originated from a total sulphur molar balance and where S is the total sulphur content in the extracted coal (wt% dry-base) and S_0 is the total sulphur content in Sulcis coal at start of the treatment. The yield of extraction (η) is calculated as ratio of the weight of treated coal with that of the original one.

KOH solution reacts preferentially with organic sulphur, whereas the removal of inorganic sulphur from coal was best achieved with an oxidizing reagent, such as hydrogen peroxide. Actually, when the leaching agent is an aqueous solution of KOH, a substitution reaction occurs between the sulphur atom and the oxygen atom in the carbonaceous matrix. For this reason, the leaching with this reagent for times greater than 9 h caused a significant reduction of organic sulphur in Sulcis coal, though accompanied by a drastic reduction of the sample. A darker color of the said aqueous solution took place after treatment with KOH solutions, and this is due to outlet of potassium humates. It has been reported (Lolja, 1999) that the extraction of humic acids by alkaline-air oxidation out of low rank coals increase a little after 4 hours at low temperature. However, after the H_2O_2 reaction, the color of the said solutions changed from light yellow to brown, depending on the hydrogen peroxide concentration and treatment time. Moreover, hydrogen peroxide reacts vigorously and exothermically with coal. As soon as the slurry is warmed, an effervescence develops, apparently due to catalysis by coal constituents (probably pyrite) of the breakdown of H_2O_2 to CO_2 and water. In literature is reported (Antonijevic et al., 1996) that sulfuric acid dilute solutions are able to stabilize this reagent.
The disulfide in pyrite can be oxidized to elemental sulphur. Essentially, the possible reaction involving pyrite oxidation is the following:

$$[O] + FeS_2 = Fe^{+2} + 2S + [O^{-2}] \tag{2}$$

The tests conducted have verified the technical efficiency of the process for desulphurization of Sulcis coal. The results of experimental tests for KOH leaching step are given in Table 1, whereas the results of the best experimental tests for H_2O_2 leaching step, which were conducted at 40 °C, are given in Table 2.

Table 1: First leaching step (KOH aqueous solution) experimental results

Reaction Time [min]	Yield of extract. (η)	Sulphur conv. (Xexp)	Sulphur [%wt.]
0	1	0	5.97
15	1	0.080	5.49
30	0.997	0.100	5.39
60	0.994	0.115	5.32
120	0.990	0.130	5.25
300	0.983	0.150	5.16
360	0.973	0.170	5.09
420	0.960	0.175	5.13
480	0.947	0.180	5.17
540	0.932	0.181	5.25

Table 2: Second leaching step (H_2O_2 aqueous solution at 40°C) experimental results

Reaction Time [min]	Yield of extract. (η)	Sulphur pyr. conv. (Xexp)	Sulphur pyr. [%wt.]
0	1	0	1.900
15	0.99	0.209	1.518
30	0.97	0.337	1.298
60	0.95	0.511	0.978
90	0.9	0.610	0.823
120	0.88	0.674	0.704
180	0.86	0.757	0.537
240	0.85	0.805	0.436

3.1 Kinetic model for KOH leaching step

In the present work, in order to describe the first leaching step of Sulcis coal, we reports a model, which has been yet reported in literature. Figure 2 shows the good accuracy of this model in fitting our experimental results (correlation coefficient, r = 0.998). Actually, as Lolja (1999) have explained, the desulphurization mechanism in terms of total sulphur, for this leaching step, is well described by the model of unreacted-shrinking core in a homogenous coal particle of unchanging size during process development. According to this model, a chemical reaction component was considered during diffusive flow of KOH through particle pores, whereas the external diffusion stage might be omitted when modeling this process.

3.2 Kinetic model for H_2O_2 leaching step

The kinetics of the removal of pyritic sulphur from Sulcis coal is well described by using a continuous reaction model. In fact, as Ahnonkitpanit et al. (1989) have reported, the rate of reaction for this oxidizing agent was found to be well fitted by this kind of kinetic model, that was second order with respect to pyritic sulphur.

Figure 3 presents the linearised Arrhenius plot (r = 0.997), at different temperatures. The regression analysis of the kinetic data allowed us to obtain the rate constants at different temperatures.

From the regression analysis experimental results allowed us to obtain the following equation for Sulcis coal:

$$k = (8 \cdot 10^{-1}) \cdot \exp\left[\frac{-16.5 \cdot 10^{-6}}{RT}\right] \tag{3}$$

As the below equation shows, Sulcis coal is a relatively young coal; for this reason it presents a high porosity. This characteristic justifies the low value calculated for its activation energy (Ea = 16.5x10^{-6} J/kmol) into the expression of the rate constants, compared to the values of the same parameter for other coals (Ahnonkitpanit et al., 1989) which are reported in literature.

4. Conclusions

Previous works (Carbini et al., 1990; Fois et al., 2010) analyzed chemical cleaning and sulphur removal from Sulcis coal, in order to optimize the environmental impact concerning the use of this coal. This last work shows a more economic pre-combustion cleaning method, due to the different values of some process parameters (temperature, particle size and solute concentration) compared to previous studies.

The results obtained show a desulphurization efficiency between 22.5 % and 36.58 %. Only 12 % of organic sulphur was removed, without reducing both, calorific value and material recovery of Sulcis coal. The best result, in terms of total sulphur removal, was obtained for the following conditions: treatment time 9 h for first leaching step at room temperature and 6 hours at 40 °C for the second leaching step (77 % of pyritic sulphur removal). At this conditions the efficiency of the process achieved the 36.58 %. This parameter increases as the temperature of the second leaching step increases. Actually, hydrogen peroxide decomposition accelerates at 40 °C (Antonijevic et al., 1996).

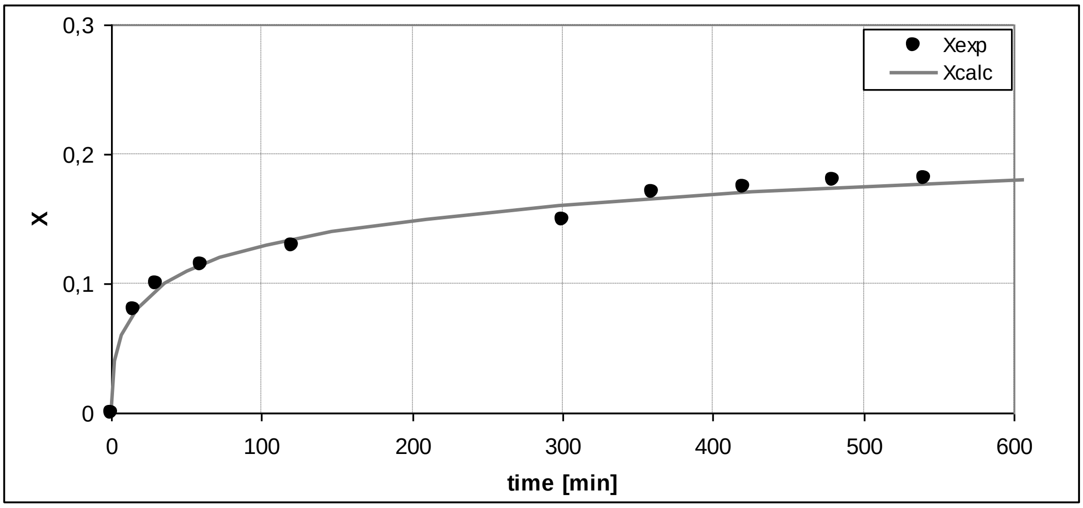

Figure 2 Total sulphur conversion vs. treatment time for Sulcis coal leaching with KOH

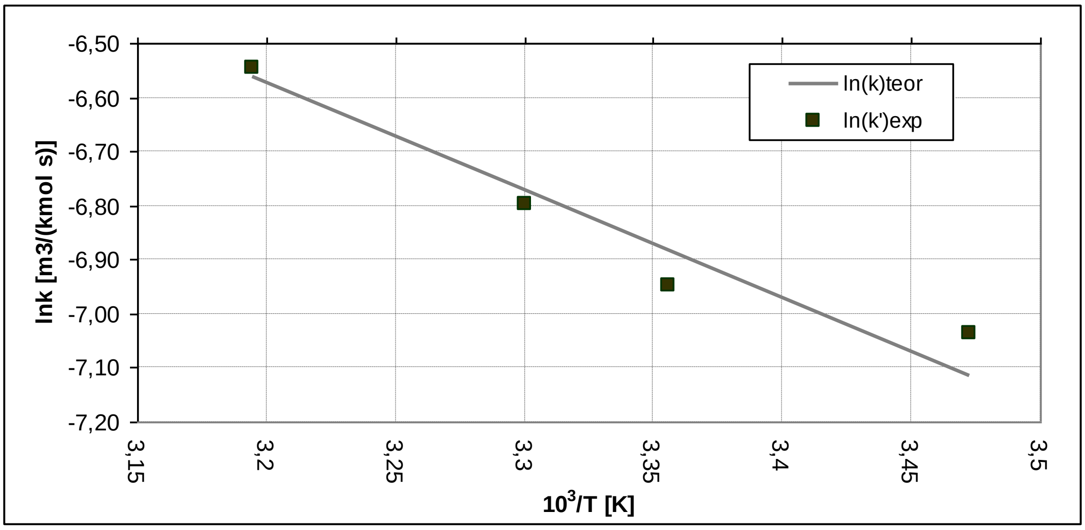

Figure 3 Arrhenius plot for pyritic sulphur reaction with H_2O_2 in Sulcis coal.

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