Sulphur Removal From Sulcis Coal By Sequential Leaching With Koh Followed By H_2O_2

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The present work shows the results of the experimental tests conducted on Sulcis coal samples by sequential leaching of potassium hydroxide followed by hydrogen peroxide. The tests carried out verify the technical efficiency of the process for desulphurization of that coal. Sulcis coal is a sub-bituminous coal from the Monte Sinni mine in the South West part of Sardinia island, Italy. The ash content of this coal is about 15 wt % as received, whereas the sulphur content is 7-6 wt% (inorganic sulphur is present at about 3%). The tests carried out verified the technical efficiency of the process for desulphurization of Sulcis coal. Some leaching tests allowed us to obtain a mineral fraction of about 12% and a sulphur content of about 4%.

1. Introduction

Coal is the most abundant fossil fuel on earth. In particular, semi-anthracite and anthracite are fossil coal in the real sense of the word and are the ones most exploited on a large scale, being the richest in carbon content and hence provided with the highest calorific value.

However, in recent decades, one of the disadvantages related to the use of coal for energy production is the emission in the environment of sulphur oxides and hydrogen sulphide. Sulphur in coal occurs in the forms of organic and inorganic substances. The inorganic sulphur is present mainly in two forms, disulfides (pyrite and marcasite) and sulphate (mainly calcium, iron and barium). The organic form, which is bound directly to the organic coal matrix, generally occurs in the forms of thiols, sulphides, disulfides, thiophenes and cyclic sulphides.

Various methods of coal desulphurization are currently in use: physical, chemical, and biological. Since the organic sulphur is distributed through the coal matrix as an integral part of the molecular structure, its removal requires chemical treatment. However, pyritic sulphur might be removed by physical cleaning processes to different extents. Thus, there are two main coal desulphurization processes prior to its utilization: chemical processes directed usually to oxidation or reduction of sulphur; and physical processes (Kawatra and Eisele, 2001).

Many laboratory and industrial processes have been developed to partially or largely reduce the presence of sulphur through chemical processing and a large number of papers is available on literature about these techniques. Experimental tests involve mainly strong mineral acids (such as Hydrochloric, Nitric, Hydrofluoric, and Sulphuric Acid) and oxidizing agents (such as metallic salts, chlorine gas, peroxides, sodium hypochlorite, etc.).

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Table 1 shows the composition of the mineral matter as fraction of oxides while Figure 1 shows the XRD pattern of ash obtained by LTA and also by conventional ashing at 850°C.

The Sulcis coal, classified as sub-bituminous, has a low heating value (as received) of 20.14 – 21.76 MJ/kg. Since most of the pyritic sulphur is finely disseminated in crystals of micron or sub-micron size (Carbini et al., 1990), the only remaining possibility of removing sulphur from this coal prior to its utilization is confined to chemical methods.

Figure 1 XRD spectrum of Sulcis coal ash obtained by low and high temperature methods
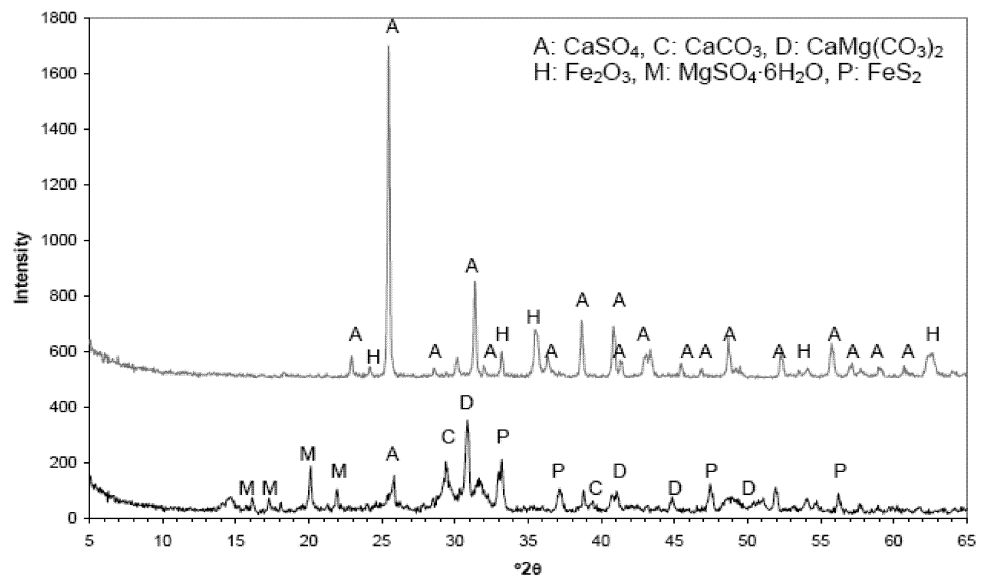
Table1 Composition of the mineral matter as fraction of oxides (Analysis XRF)

Parameter	[wt%]
SiO_2	28.80
Fe_2O_3	24.15
MgO	0.72
CaO	20.88
Al_2O_3	18.00
Na_2O	0.95
TiO_2	0.68
K_2O	0.65
SO_3	5.17

2. Experimental

Sulcis coal with particle size < 5 mm was treated with a single-stage KOH leaching solution, with a single-stage H_2O_2 leaching solution, and with a two-stage leaching sequence of aqueous solution of KOH followed by aqueous solution of H_2O_2.

Leaching experiments 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. The effect of leaching agents, concentration of the leaching solutions, temperature and residence time in the reactor were investigated. The removal of both, inorganic sulphur and ash from coal was best achieved with an oxidising reagent, such as hydrogen peroxide. The tests conducted verified the technical efficiency of the process for demineralization and /or desulphurization of Sulcis coal. Actually, some leaching tests allowed us to obtain a mineral fraction of about 10% and a sulphur content of about 4%.

The first leaching step was carried out using KOH aqueous solution at a 95°C temperature for 6 hours while the second leaching step was performed either with a 3.5 wt% aqueous hydrogen peroxide solution at a temperature of 90°C for 6 hours, or using a 10 wt% or a 20 wt% aqueous hydrogen peroxide solution stabilized with 0.2M aqueous sulphuric acid solution at room temperature for 2 hours.

After completion of the reaction, the mixture was recovered and the coal was separated from the leaching solution using a filtering paper. The soluble residues remaining in the product were dissolved by washing them with 500 ml of distilled water. The final solid product was then dried and analysed.

The calorific value was determined by a high-pressure oxygen bomb calorimeter (LECO AC 500). A 1g approx. weight coal sample was required for the determination. Ash analyses were performed by a Thermo Gravimetric Analyser (MAC 400). Total sulphur content was determined by a sulphur analyzer (SC132). The Oxygen content was then inferred by difference.

3. Results and discussions

A previous work (Mura et al., 2005) applied the results found in the literature to assess the effects of leaching with mineral acids on Sulcis coal.

Carbini et al. (1990) believe that low rank coals show a significant reduction in calorific value probably because they contain a higher number of carboxylic and phenolic groups than the higher rank's, which increase the solubilization of such coals in the caustic mixture. Moreover, the effect of the mechanical disintegration following the chemical attack, contributes to further increase losses in calorific value. This disintegration generates the formation of ultra-fine coal particles, a phenomenon more remarkable in the lower rank coals, more porous than the higher ones, where consequently the calorific value loss becomes quite considerable.

Therefore Carbini et al. (1990) conclude stating that the use of a caustic mixture in the process is not suitable for low rank coals, because the high loss of calorific value makes the process itself economically unacceptable.

Table 2 shows chemical analysis of the initial untreated sample of Sulcis coal.

Table 3 shows the Ash, S contents, yield of extraction and LHV of Sulcis coal which is untreated, treated with KOH, treated with H_2O_2, and treated with KOH followed by increasing concentrations of H_2O_2.

Table 2 Analysis of untreated Sulcis coal (a.r.)

Proximate Analysis	[wt%]
Moisture	12.79
Fixed Carbon	35.02
Ash	13.16
Volatile matter	39.03
Ultimate Analysis	[wt%]
C	53.64
H	4.84
N	1.28
S	5.97
O_2[diff]	13.16
Moisture	8.32
Sulphur Forms	[wt%]
$S_{pyritic}$	1.9
$S_{organic}$	3.96
$S_{sulphate}$	0.11

Table 3 Ash, S contents, yield of extraction and LHV of Sulcis coal (a.r.) treated with KOH aqueous solutions followed by H_2O_2 aqueous solutions

Sulcis Coal sample	1st step leaching solution	2nd step leaching solution	Ash [wt%]	S [wt%]	η [-]	LHV [kcal/kg]
Untreated	-	-	13.16	5.97	-	5196
One step leaching	KOH (6 h, 16 wt%, 95°C)	-	18.33	3.04	1.05	3993
One step leaching	H_2O_2 (2h, 10 wt%, 25°C)	-	12.23	5.55	0.96	5395
One step leaching	H_2O_2 (2h, 20 wt%, 25°C)	-	11.67	5.4	0.9	5398
Two step leaching	KOH (6 h, 16 wt%, 95°C)	H_2O_2 (2h, 20 wt%, 25°C)	13.71	4.12	0.98	4.988
Two step leaching	KOH (6 h, 10 wt%, 95°C)	H_2O_2 (2h, 10 wt%, 25°C)	15.42	4.27	0.99	4847
Two step leaching	KOH (6 h, 16 wt%, 95°C)	H_2O_2 (6h, 3.5 wt%, 90°C)	17.49	4.15	1.00	4715

The yield of extraction (η) is calculated as the ratio of the weight of treated coal with the weight of the original one.

After treatment with KOH solutions a slight darkening of the solution appeared, due to low temperature and low outlet of potassium humates. It has been reported (Saimir A. Lolja, 1999) that the extraction of humic acids by alkaline-air oxidation out of low rank coals slightly increases after 4 hours at low temperature, while sulphate and pyritic sulphur were able to react with KOH and moved to filtrate.

The removal of pyrite from coal is best achieved with an oxidizing reagent, such as hydrogen peroxide. The possible reaction involving pyrite oxidation is the following:

$$[O] + FeS_2 \rightarrow Fe^{+2} + 2S + [O^{-2}] \tag{1}$$

However, KOH solutions react preferentially with organic sulphur. 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. This reaction causes a dramatic loss of the calorific value of the Sulcis coal (LHV = 3993 kcal/kg; S = 3.04%).

In order to limit the calorific value to decrease, which would result from an exclusively basic attack, hydrogen peroxide is used as oxidizing agent at different concentrations and temperatures. It is observed that the use of hydrogen peroxide increases the calorific value of Sulcis coal, due to the decrease of ash (demineralization), and that increase is directly linked to the concentration of hydrogen peroxide in the leaching solution.

4. Conclusions

No processes are known up till now, which allow low-medium rank coals to be treated, so that all the requirements necessary to make their desulphurization effective and economically advantageous are simultaneously satisfied.

The object of the present work is the desulphurization of low-medium rank coal in an efficient and highly reproducible way, whereas limiting as far as possible the loss of calorific value, in order to upgrade low-medium rank coal and make economically and environmentally affordable its use.

In the present work the effects of leaching agents, concentration of the leaching solution, particle size, temperature and residence time in the reactor were investigated. The results of the experimental tests show that the removal of inorganic sulphur from coal was best achieved with an oxidising reagent, such as hydrogen peroxide. We performed both singular and double leaching steps. Since the treatment of Sulcis coal toward caustic solutions causes a drastic loss in the calorific value, we preferred to use hydrogen peroxide as second leaching agent for two-step processes.

Moreover, the tests carried out, verified the technical efficiency of the process for demineralization and desulphurization of Sulcis coal. Actually, some leaching tests allowed us to obtain a mineral fraction of about 12% and a sulphur content of about 4%.

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