CHEMICAL BENEFICIATION OF LOW GRADE COAL
– A REVIEW

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Abstract:

India is having large reserves of low grade coals. The use of low-grade coal in various industries like power plants, metallurgical plants, cement units etc. leads to environmental pollution because of generation of large amount of solid and gaseous pollutants. Therefore, it is of importance paramount to clean the coal before its utilization. There are a number of upgrading technologies to produce clean coal. The current paper reviews demineralization aspects by physical and chemical beneficiation of high ash and sulfur containing coal. Physical beneficiation of coal is not very effective in separation of the finely dispersed minerals, whereas chemical beneficiation uses expensive reagents and leads to generation of large amount of wastewater which needs to be purified before discharge. Thus, a combined approach consisting of physical and chemical cleaning of coal appears to have a potential for significant reduction of ash with less investment while generating less polluting wastewater.

Keywords: Coal; Chemical beneficiation; Physical beneficiation; ash.

1. INTRODUCTION

Coals which are low in specific energy because of high moisture content and / or high ash/ sulfur contents, and produce emissions of concern are termed as low grade coal. Coal generally incorporates various amounts of mineral matter as impurity. The presence of mineral matter adversely affects most aspects of coal utilization and processing. Therefore, removal of mineral matter prior to coal utilization is desirable. Sulfur both in inorganic and organic forms is deleterious in coal which releases SO₂ during burning. Therefore, it is necessary to demineralise and desulfurize such coals prior to utilization for its economical and environmental benefits.

India is having a large reserves of coal concentrated mainly in the east and north-east region of India. The quality of coal is poor in comparison to that of other countries due to higher ash content and low calorific value. This is because Indian coals are typically of drift origin and the mineral matters are finely distributed inside the coal matrix and at times firmly bound. The mineralogical analysis of Indian coals shows the presence of mineral matter in the form of kaolinite, quartz and clay. The indigenous coals have an average GCV (gross calorific value) of 3500-4000 kcal/kg and ash content of 30-50% as compared to the overseas coal (GCV = 6000 kcal/kg, ash = 8-10%). The high sulfur and ash content restricts large scale utilization of Indian coal. Demineralization prior to utilization is an effective way to reduce ash content of coal and ensure environmental friendly coal combustion process.
The mineral matters associated with coal are of two types — one is chemically bonded with organic matter and the other exists as separate entity. Demineralization and desulfurization of coal may be achieved by both physical and chemical methods. Some demineralization can be achieved with simple physical processes based on the difference in the density and surface properties of the mineral and carbonaceous parts of the coal. Physical processes are cost effective but may not be effective in separation of the finely dispersed minerals and those bound to the coal structure. The chemical methods for the demineralization of coal have some advantages because both types of mineral species can be leached out. However, the extent of demineralization depends on the nature of the associated minerals and the reagent used.

2. PHYSICAL BENEFICIATION OF COAL

The role of coal cleaning for the removal of toxic elements was discussed by Akers and Dospoy, 1994 in greater depth. Coal cleaning as a means of abating emission of potential trace elements offers the advantages of relatively low cost, improved boiler thermal efficiency and reduction of SO₂ emissions. However, physical cleaning is unlikely to provide complete removal of the trace elements. Physical treatment includes flotation, magnetic separation or the use of hydrocyclones which mainly removes inorganic sulfur, whereas elimination of organic sulfur requires in most cases chemical and/or microbial treatment [Palmer et al., 1995].

Primarily, the ash and sulfur-bearing minerals found in coal are hydrophilic, and therefore should remain in the tailings in flotation. Flotation has been an established technique for processing fine coal of < 0.5 mm size. However, efficiency of the process depends on the hydrophobicity of particles - even small portion of coal matter in the gangue would be a great loss [Özgen et al., 2009]. Again flotation reagent cost adds up to the processing cost which makes the flotation method more expensive than other physical methods. Yet, to remove inorganic materials viz. pyritic sulfur, the most suitable one is flotation to clean coal [Demirbas, 2002].

The effect of pH, collector (kerosene) amount, and frother type (MIBC, AF 76, pine oil, DF 250) for depressing pyrite from the Hazro coal was investigated by Ayhan et al., 2005. The best flotation conditions were found to be: pH 9; kerosene amount 250 g/t; and MIBC frother type. The flotation method reduced ~ 50% ash along with most of sulfate sulfur (>90%) and 66.9% of the pyritic sulfur from the coal sample. Column flotation has an advantage over conventional flotation as it can provide higher concentrate grade and recovery, lower maintenance costs, and improved process control [Groppo and Parekh, 1990]. Flotation variables are the pH of pulp, types and dosages of reagents, percentage of solid in pulp, temperature and agitation rate [Cilek et al., 2000].

Among the physical methods, the oil agglomeration process [Tsai, 1982] has drawn special attention in recent years. A physical method of cleaning Assam coal from India by agglomeration with xylene and hexane was reported by Baruah et al., 2000. The maximum organic matter recovery for xylene has been found to be 92% whereas with hexane the value is about 55% on a dry basis. The highest ash rejection values with xylene and hexane are almost same (90%).

Surface based separation processes such as froth flotation and oil agglomeration have been traditionally recognized as the practical methods for cleaning fine coal. These processes are very selective in rejecting well liberated mineral matter, but are much less effective if the feed coal contains a disproportionate amount of
composite particles. Pyrite cannot be floated if the surface chemistry of the flotation pulp is not properly controlled. The beneficiation of two lignite tailings, containing 66 and 53% ash, by Multi Gravity Separator (MGS) was investigated by Özgen et al., 2011. It was possible to produce cleaner coals containing ~ 23% and 22.9% ash with a recovery of 49.3% and 60.01% respectively.

Most of the coals present in India are of low grade with high mineral matter varying from 15% to greater than 50%. Since the washability characteristics of Indian coal is not good, it is difficult to remove the mineral matter by conventional techniques based on specific gravity difference such as heavy separation and surface dense media such as flotation to produce low ash coals for coke making and power generation [Dash et al., 2012].

3. CHEMICAL BENEFICIATION OF COAL

Due to low demineralization by physical techniques to produce ultra clean coal (UCC), chemical processes are frequently considered. The general approach followed to upgrade low grade coal has involved leaching under a variety of conditions. Chemical cleaning of coal with alkali and acid solutions has proved effective in reducing significant amounts of ash-forming minerals, pyritic sulfur and organic sulfur (disulfides, thiols, sulfides, thiophenes and thioketones) from coal. Chemical demineralization processes, either alone or following physical cleaning processes, are used extensively in the production of UCC. The chemical demineralization processes which have been investigated, include leaching with NaOH [Mukherjee and Borthakur, 2001], Ca(OH)₂ [Wang et al., 1996], Na₂CO₃ [Adeleke, 2011], mineral acids viz. HNO₃ [Steel and Patrick, 2003], HCl [Alam et al., 2009], HF [Steel et al., 2002], H₂SO₄ [Paul et al., 2006], oxidizing agents viz. H₂O₂ [Karaca and Ceylan, 1997], FeCl₃ [Vasilakos and Clinton, 1984], Fe₂(SO₄)₃ [Meyers, 1975], K₂Cr₂O₇ [Ali et al., 1992], NaOCl [Li and Cho, 2005], mixture of HF and HCl [Steel et al., 2001], NaOH and KOH [Mukherjee, 2003] and sequential leaching by NaOH-H₂SO₄ [Nabeel et al., 2009].

3.1 Acid Leaching

Direct acid leaching is a powerful method to demineralise coals, as summarized in Table-1. A few compounds are dissolved in caustics, but low pH is generally favourable for metal ion solubilisation.

Concentrated HI was used to remove sulfate and pyritic sulfur in Spanish coals at temperatures up to 260°C and pressures up to 60 bar in a microwave heating set up [Andres et al., 1996]. Inorganic sulfur was completely removed in the first 10 min of the treatment while 70% of the organic sulfur could be removed only after 20 min. Use of other acids showed low yields.

HF can effectively dissolve quartz and kaolinite. Quartz is more difficult to mobilize than kaolinite, therefore, coal demineralization rate strongly depends on the proportion of quartz and kaolinite in a coal [Wang and Tomita, 1998]. The demineralization of bituminous coal of UK using a two-stage leaching by hydrofluoric acid and ferric nitrate [Wu and Steel, 2007] showed decrease in ash content from 5.3% to 990 ppm. In first-stage with HF at 65°C reduced the ash content to 1.37% by mainly removing Al and Si containing minerals and subsequent leaching by ferric ions decreased the ash content further to 990 ppm by removing most of the pyrite and fluorides formed during the HF leaching. In a chemical cleaning process (the Meyers process), crushed coal was leached with an acidic solution of ferric sulfate at 100-130°C for several hours [Meyers, 1977]. It removed almost all pyritic sulfur.
A two stage leaching sequence of aqueous HF and HNO₃ was proposed by Rubiera et al., 2003 for coal demineralization. The chemical treatment of a high-volatile bituminous coal with 25% HF for 8 h at 60°C followed by 25% HNO₃ for 16 h at 60°C reduced the ash content from 6.2 to 2.2% and then to 0.3% respectively.

Table 1: Chemical Beneficiation of some coal samples

<table>
<thead>
<tr>
<th>Ash Type</th>
<th>Coal type, place (% ash, % S)</th>
<th>Leaching media &amp; Conditions</th>
<th>Highlights [% deashing/desulfurization]</th>
<th>References</th>
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<tr>
<td>High ash</td>
<td>(i) Bituminous coal, Amasra, Turkey (44-69% ash, 0.21-0.73% S)</td>
<td>Size: 140-500 µm, 0.5N NaOH – 10% HCl, [S/L: 1: 16, 20 min]</td>
<td>46.6% Demineralization</td>
<td>Bolat et al., 1998</td>
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<td></td>
<td>(ii) Coking coal (33.6% ash) &amp; power grade coal (43% ash), Topa, Jharkhand, India</td>
<td>Size: 125-250 µm, 20% NaOH – 10% H₂SO₄ [S/L: 3:50, 24 h]</td>
<td>75-80% Demineralization</td>
<td>Nabeel et al., 2009</td>
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<td></td>
<td>(iii) Coking coal, Lafia-Obi, Nigeria (32.5% ash)</td>
<td>Size: ±250 µm, H₂O-Na₂CO₃-H₂O [90°C, 25 min]</td>
<td>38.9% Deashing, 19.9% final ash.</td>
<td>Adeleke et al., 2011</td>
</tr>
<tr>
<td>Medium ash</td>
<td>(i) Subbituminous coal, Tabas Iran (16.8% ash, 1.76%S)</td>
<td>30% HCl &amp; 30% HNO₃ [90°C, 90 min]</td>
<td>HNO₃ more effective than HCl, 53.2% deashing &amp; 75.4% desulfurization.</td>
<td>Alam et al., 2009</td>
</tr>
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<td></td>
<td>(ii) Subbituminous coal, (Sulcis coal), Italy (15% Ash, ~7% S)</td>
<td>Size: &lt;5 mm, 1st step-KOH [S/L:2/5, 95°C, 6h] 2nd step - 3.5% H₂O₂ [S/L: 2.5, 90°C, 6 h]</td>
<td>Loss of caloric value with KOH, 12% final ash and 4% S.</td>
<td>Fois et al., 2010</td>
</tr>
<tr>
<td></td>
<td>(iii) Subbituminous HV coal, Thailand (14.7% ash, 4.2%S)</td>
<td>Size: 500-1000 µm, 2% Methanol &amp; 0.025g KOH/g coal [S/L: 2:3, 150°C, 60 min]</td>
<td>58% Sulphur and 24% ash removed</td>
<td>Ratanakandil ok et al., 2001</td>
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<td></td>
<td>(iv) Low grade coal, Degari, Pakistan (145 ash, 3% S)</td>
<td>Size: 250-212 µm, EDTA, citric acid, HCl, HNO₃ &amp; acid mixture of H₂O, HNO₃, HCl and HF (10:5:1:1) [S/L: 1:110, 50°C, 5h]</td>
<td>64-71% Deashing by HCl, HNO₃ &amp; acid mixture, 64% deashing by EDTA &amp; citric acid. No carbon loss.</td>
<td>Shakirulrhel et al., 2008</td>
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<td>Low ash</td>
<td>(i) Coking coal, Tirap, Assam, India (6.60% ash)</td>
<td>Size: 212-600 µm, 500g/L NaOH [S/L: 1:10, 120°C, 120 min]</td>
<td>~70% Demineralization.</td>
<td>Kumar and Gupta, 1997</td>
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<td></td>
<td>(ii)Bituminous coal, Harworth, UK (5.30% ash)</td>
<td>Size: &lt;52 µm, 1st stage: 3.51 M HF [S/L: 3/10, 65°C, 4h] 2nd stage: Fe(NO₃)₃ [S/L:1:10, 100°C, 6h]</td>
<td>1st stage: 1.37% ash 2nd stage: 990 ppm ash.</td>
<td>Wu and Steel, 2007</td>
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<td></td>
<td>(iii) Victorian Brown coal for gas turbine [Coal A: 1.65% ash, 0.5% S] [Coal B: 2.35% ash, 0.8% S]</td>
<td>Size: 106-150 µm, 1M pyroligneous acid &amp; citric acid and 0.1M Na-EDTA [S/L:1:10, 24h] 1M ammonium acetate-1.5M HNO₃ [24 h]</td>
<td>Ultra-clean coal by using cheap and weak acids.</td>
<td>Wijaya et al., 2011</td>
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</table>

Steel and Patrick, 2001 investigated the production of UCC by chemical demineralization of a high-volatile British coal containing 7.9% ash and 2.6% sulfur by leaching with HF followed by HNO₃ solutions. Upon treatment for 3 h at 65°C, HF reduced the ash content to ~2.8% and the subsequent treatment with HNO₃ reduced the ash content to 0.63% by dissolving fluoride compounds and iron from FeS₂. The remaining ash consists largely of unreacted FeS₂ encapsulated in the coal structure. This investigation shows that HNO₃ reacts with FeS₂ above a particular HNO₃ concentration and is consumed preferentially to a certain extent.
with the organic coal structure. The final sulfur content following treatment with HF and HNO$_3$ was found to be 1.4%. In a separate study [Steel and Patrick, 2003] ash content was reduced from 5 to 0.2% and sulfur from 2.4 to 1.3% by a sequential leaching with HF and HNO$_3$. Producing ultra clean coal by microwave pre-treatment and sequential leaching with HF and HNO$_3$ was reported [Jorjani et al., 2011].

Rodriguez et al., 1996 concluded that nitric acid leaching of Spanish coal at atmospheric pressure is effective for desulfurization of intermediate-rank coal, especially for inorganic sulfur removal. In another study [Rodriguez et al., 1997] it was found that most of the sulfur reduction takes place during the first 5 min. At 90°C, the total sulfur content was quite below the initial organic sulfur content. Alvarez et al., 2003 observed that HNO$_3$ leads to a rapid reduction of pyritic and sulfate sulfur, however, FT–IR results of coals leached at high temperatures by this acid showed that the oxidization capacity of coal increased and the O$^-$ of nitrate group appeared as carbonyl group in molecular structure of coal. Nitrogen substitutes the two adjacent nonbonding hydrogen atoms and nitrates the coal as aromatic nitrogen. For this reason the leaching process with nitric acid is avoided to preserve desirable characteristics and appearance of coal.

Steel et al., 2001 investigated the leaching behaviour of the mineral matter in coal towards aqueous HCl and HF. HCl was found to dissolve simple compounds such as phosphates and carbonates, but it could not completely dissolve the clays. HF reacts with almost every mineral matter except pyrite. Desulfurization of Tabas Mezino coal was conducted with two consecutive steps of froth flotation at ambient temperature followed by leaching with nitric acid [Alam et al., 2009].

Mineral acids for demineralization of coal, can modify the surface morphology and harm carbon while reducing the calorific value and creating environmental problems due to their strong oxidizing power. Therefore, some mild leachants were considered for deashing of coal, to avoid above disadvantages [Shakirullah et al., 2006]. EDTA and citric acid were found as effective as mineral acids like HCl, HNO$_3$, HF etc. The use of cheap and weak acids such as pyroligneous acid and citric acid for the generation of ultra-clean coal had proven effeciencey [Wijaya et al., 2011]. Compared to ammonium acetate, these acids even contained substantial amount of chelating agents to mobilise the nitric acid-insoluble oxides/hydroxides in coal, which in turn substantially reduced the ash and even sulfur / chlorine contents.

Leaching of various metals from coal into aqueous solution containing an acid or a chelating agent was investigated by Ohki et al., 2004; demineralization was found to increase with the increase in HNO$_3$ or EDTA concentration. Interestingly even a low concentration of EDTA (0.1mM) had a considerable ability of demineralization.

The effect of hydrogen peroxide alone and in presence of dilute sulfuric acid on desulfurization and demineralization of coal of north-eastern region, India was investigated by Mukherjee et al., 2001. H$_2$O$_2$ (15%) alone removed over 76% pyritic sulfur, 70% sulfate sulfur, 5% organic sulfur and over 14% ash at 25°C which improved to almost complete removal of pyritic and sulfate sulfur, over 26% organic sulphur and 43% ash in the presence of 0.1 N H$_2$SO$_4$. Sulfuric acid acts as catalyst for bringing oxygen and pyrite molecules close to each other which helps in desulfurization. The kinetic and energetic studies on the acidic (0.1 N H$_2$SO$_4$) hydrogen peroxide desulfurization of Indian coal were reported by Mukherjee and Srivastava, 2004.
Vasilakos et al., 1984 investigated chemical beneficiation of high volatile bituminous coal with H$_2$O$_2$/H$_2$SO$_4$ at ambient temperature. Almost complete removal of inorganic sulfur and substantial reduction in ash were observed. However, organic sulfur was hardly affected. Aphonkitpanit and Prasassarakich, 1989 followed the similar treatment for subbituminous high volatile coals from Thailand and observed removal of a small amount of organic sulfur (7.1%) along with most of the ash and inorganic sulfur. Karaca and Ceylan, 1997 also found H$_2$O$_2$ as an effective agent for removal of ash and pyritic sulfur, but less effective for organic sulfur. A 15% H$_2$O$_2$ was suitable for appreciable reduction in ash and pyritic sulfur from lignites within 60 min at 30°C.

3.2 Alkali Leaching

In alkali leaching process the dominant kaolinite and quartz phases in coal are converted to hydrated alkali-bearing silicate and alumina-silicate complexes like sodalite etc. A portion of pyrite and organic sulfur can also be removed.

The demineralization of coal with aqueous alkaline solution is reported [Yang et al., 1985; Kara and Ceylan, 1988; Mazumdar and Sengupta, 1980; saydut et al., 2011]. Yang et al., 1985 reported improved demineralization with increase in temperature, time and NaOH concentration and decreased particle size of coal. Kara and Ceylan, 1985 have reported similar results for demineralization of Turkish lignites with NaOH.

The effect of aqueous caustic leaching (ACL) of asphaltite from Turkey was investigated by Saydut et al., 2011. Caustic leaching at 180°C for 16 h reduced the ash content of asphaltite by 44.6%, pyritic sulfur by 83.3%, organic sulfur by 53.9%, total sulfur by 61.82% and volatile matter by 46.29%. Similarly Friedman and Warzinski, 1977 achieved complete removal of pyritic sulfur and 40% organic sulfur from coal by treatment with sodium hydroxide solution at 300°C. Chemical treatment of coal by grinding and aqueous caustic leaching was studied by Balaz et al., 2001.

Molten caustic leaching (MCL) process is effective in reducing significant amounts of ash-forming minerals, pyritic sulfur and organic sulfur from solid fossil fuels. Removal of inorganic components from fuel by MCL can be expressed as:

$$\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$$  
(1)

$$4\text{FeS}_2 + 20\text{NaOH} \rightarrow 4\text{NaFeO}_2 + 8\text{Na}_2\text{S} + 10\text{H}_2\text{O} + \text{O}_2$$  
(2)

Sodium silicate and sodium iron oxide can thus be easily removed by water leaching while regenerating spent alkali [Yaman and Kucukbayrak, 1999]. The alkaline desulfurization is more effective in removing pyritic sulfur than organic sulfur; ~50% of total sulfur can be easily removed [Lolja, 1999].

Effect of alkali treatment for ash and sulfur removal from Assam coal, India was investigated by Mukherjee and Borthakur, 2003. Chriswell et al., 1989 ; 1991 stated that the chemical cleaning of coal by MCL can remove over 95% of the ash-forming minerals and up to 90% of sulfur from coal. However, during MCL unwanted carbonate by-products are formed which result in the loss of coal carbon, significant consumption of expensive caustic, and subsequent filtration problems during the processing of spent caustic solutions. Lee and Shon, 1997 have also reported large reductions in sulfur and ash by MCL. Araya et al., 1981 achieved reduction of 29% ash and 30% total sulfur from a subbituminous coal from Chile by treatment with 10% sodium hydroxide solution at 80°C for 8 h. Wang et al., 1986 applied caustic wash to two different coals, one
with high ash (15.5%) and the other with low ash content (7%). Removal of major components, quartz and kaolinite was easy, whereas the removal of Ca and Fe compounds strongly depended on the type of mineral matter. Coal mineral matter can react with fused or molten caustic at 370°C in a much shorter time of heating than that commonly used in the MCL process for chemical cleaning of coal [Kaushik et al., 1988]. However, the MCL treatment is a harsh process, and results in a partial conversion of the coal to volatile and produce changes in the coal structure. Therefore, the aqueous caustic process with lower operating conditions, will have practical value.

The use of calcium oxide (lime) instead of sodium hydroxide was attempted as a leaching reagent for Australian coal [Wang et al., 1996; 1997, Wang and Tomita, 1997]. Lime (Ca(OH)₂) is efficient and cost effective when compared with NaOH. Other advantages of using lime instead of sodium hydroxide are: (1) less extensive extraction of coal organic matter into the leaching solution; (2) less corrosive to the reactor and equipment materials; and (3) a lesser fouling effect of the residue if chemically treated coal is employed in combustion or gasification applications. Wang and Tomita, 1997 investigated the chemistry of hydrothermal reactions of Ca(OH)₂ with pure quartz and pure kaolinite. Wang et al., 1996 found that about 76% of ash was removed from Newstan coal from Australia by leaching with 5% CaO at 340°C for 120 min, followed by hydrochloric acid washing; the ash content decreased from 9.2% to 2.2%. Stambaugh et al., 1975; Stambaugh, 1977a, 1977b; used a mixture of 10% NaOH and 2-3% Ca(OH)₂ as a leaching agent. This process needed fairly rigorous leaching conditions: 250-300°C and 3.9-8.4 MPa pressure. The calcium added acts as a sulfur scavenger when the treated coal is burnt.

Recently, the response of Nigerian coal to de-ashing with Na₂CO₃, a cheaper alternative to sodium hydroxide was investigated [Adeleke et al., 2011] with average ash reduction of 38.66%. A complete removal of inorganic sulfur and about 70 wt.% reduction in organic sulfur from coal were achieved with dilute solution of Na₂CO₃ at temperatures between 120-150°C under pressure [Markuszewski et al., 1978]. Norton et al., 1987 reported removal of 60 - 90% ash and sulfur from some bituminous coals from New Zealand using fused caustic. Markuszewski et al., 1985 treated several bituminous coals with molten mixtures of NaOH and KOH at 350-370°C and could remove 80-90% ash and 70-80% of total sulfur. In TRW Gravimelt process revealed that mixtures of NaOH and KOH rather than NaOH alone desulfurized coal (>90% total sulfur) more efficiently at 623 K [Kusakabe et al., 1989].

3.3 Leaching of Coal with Alkali Followed by Acid

The approach of alkali leaching in combination with acid washing has been universally studied. One reason is that the leaching agents like NaOH and KOH are extremely effective to remove most of the minerals from coal. The dominant kaolinite and quartz in coal are converted to hydrated alkali-bearing silicate and alumina-silicate complexes (e.g., sodalite), a portion of pyrite and organic sulfur can also be removed. The products formed from alkali treatment are weakly soluble and hence essentially needs treatment by dilute acid.

The effects of hydrothermal leaching using solutions of either sodium hydroxide or nitric acid has been reported by Blanchard et al., 1995. The caustic wash applied to two different lignites from Turkey [Çulfaz et al., 1996]. A high temperatures (460 K) ~90% of the mineral matter was removed by washing with caustic solution followed by acid washing
for both low ash and high ash coals. The caustic-HF leaching method had been found to be the most effective method for coal de-ashing, followed by caustic-HCl-HNO₃ and caustic-HCl-H₂SO₄ leaching methods [Kumar and Shankar, 2000].

The effect of leaching asphaltite samples from Turkey with molten NaOH followed by mild acid leaching was investigated by Duz et al., 2008. The complete removal of pyritic sulfur, 70% organic sulfur and ash and 70-79% volatile matter from asphaltites was reported with alkali at a 1:1 ratio with asphaltite at 400°C for 45 min and (1M) HCl wash. Ash content was reduced from 18.3% to 6.8% from a coal from Hazro fields Turkey and 70% of combustible was recovered with MCL [Duz et al., 2009].

Study by Mukherjee and Borthakur, 2001 showed removal of 43-50% ash, total inorganic sulfur and ~10% organic sulfur from Assam coal by treatment with 16% NaOH solution followed by 10% HCl at 90-95°C. A similar study was also carried out with KOH alone at 95 and 150°C and in combination with mild acid [Mukherjee and Borthakur, 2003]. At 150°C, successive treatments of coal with 18% KOH and 10% HCl led to 52.7% desulfurization and removed, all of inorganic sulfur and 37% organic sulfur. Deashing of sodium hydroxide leaching from Assam coking coal (Table-1) was studied by Kumar and Gupta, 1997.

Reducing the ash content of physically beneficiated Indian coals by treatment with caustic solution followed by acid washing is possible [Dash et al., 2012]. Degree of demineralization improved by increasing the reaction time, alkali concentrations and temperature, and by reducing the coal particle size. A marginal reduction in sulfur content and significant reduction in phosphorous content was observed after the acid treatment.

A process of chemical cleaning of coal by alkali-acid leaching under mild and ambient pressure was developed by Nabeel et al., 2009. Chemical demineralization of low-grade coal in a three step process using 1% or 5% aqueous NaOH treatment followed by 1% or 5% H₂SO₄ leaching has been developed with a removal of more than 75-80% of mineral matter. At CSIRO, Australia, a process have been developed [Waugh and Bouling, 1984] for removal of 90% mineral matter from bituminous coal using 10% NaOH at 200-300°C under pressure followed by acid treatment.

The effect of aqueous caustic and various acid treatments on the removal of mineral matter in asphaltite was investigated by Doymaz et al., 2007. About 59.6% of the mineral matter could be removed by 10% H₂SO₄ and 40% HF after treating with 5% NaOH solution. Similarly, Bolat et al., 1998 studied the chemical demineralization of Turkish coal using different acids (HF, HCl, HNO₃ and H₂SO₄) alone and 0.5N aqueous NaOH in combination with one or two of the acids. In another study a low level of 3.3% ash was obtained for the Tuncbilek lignite with 30% NaOH and 10% HCl [Karaca and Onal, 2003]. Baruah and Khare, 2007 reported removal of inorganic and organic sulfur and minerals by solvent extraction and alkali treatment of the coal oxidised by H₂O₂-HCOOH. Chemical leaching of high sulfur coal from Assam, India was reported by Baruah et al., 2006, besides aqueous leaching of NE coal to remove 77% sulfur in 120 h and 45°C.

4. CONCLUSIONS

It has been seen that physical processes are economical methods but are not effective in separation of the finely dispersed minerals bound to the coal structure. Some process like flotation has problem of utilising large quantities of water and results in generation of tailings as well as increase in moisture content. Whenever fine crushing is needed.
to liberate product from gangue, the more cost-effective dry fluidisation could be an alternative to the wet chemical flotation.

The mineral-rich grains may be removed by physical beneficiation and the methods developed are used commercially, but for finely disseminated minerals or organic bound elements, chemical beneficiation is an effective. However, these methods are expensive due to chemical reagents used. Almost all studies into demineralization of coal do not account for the wastewater generated and its treatment and these methods are not used industrially.

Chemical beneficiation methods may not compete with physical cleaning technologies. This is because such methods need to have low cost and be environmental friendly. Accordingly, the use of chemical methods in a hybrid approach with physical method appears to be a good option. The combined physical and chemical cleaning has been shown to be potential for deashing and demineralization of Indian coals.

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