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RESEARCH

Process engineering of demineralisation of moderate to high ash Indian coals through NaOH-HCl leaching and HF leaching

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Abstract

Chemical leaching of coals would be required to produce cleaner coals for some special applications where physical beneficiation may not be effective enough. This would also help in recovering Li and rare earth metals besides in the sequestration of CO_2. About 20 Indian coals having complexly distributed moderate to high ash contents were sequentially treated with various alkali–acid such as NaOH-HCl, HF, HCl, HCl-HF, and NaOH-HCl-HF leaching. This aimed to establish and design the best stepwise sequential process for the highest degree of demineralisation through a chemical leaching process. Kinetics and process intensification studies were carried out. More than 80% demineralisation of Madhaipur and Neemcha coals was observed using the best sequential treatment designed presently. The repeated stepwise treatment of the alkali and the acid was also studied, which was found to significantly enhance the degree of demineralisation of coals. The integrated process of alkali–acid leaching followed by solvent extraction (Organo-refining) and vice versa of the treated coal was also studied for producing cleaner coals.

Keywords Alkali–acid leaching · Demineralisation · Integrated process · Rare earth elements

1 Introduction

Coal is still the largest contributor to power generation and steel production. It is anticipated that coal will continue to supply power even after the gradual shift to renewable energy sources to stabilise the grids and economically establish carbon capture, storage and utilization technologies. However, coal remains one of the most important fossil fuels. It will likely sustain that position over the years until suitable, sustainable, environmentally sound renewable replacements are not developed. The presence of inorganic mineral matter analysed as ash and sulfur limit the use of coal along with the rise in environmental concerns. Even in India, almost 70% of the power generation is still met by coal (Giri and Sharma 2004; Meshram et al. 2015; Chakravarty and Somanathan 2021). However, Indian coals are low-grade coals because of their high ash contents. The ash contents in Indian coals vary from 5% to 55% in most Indian coals with an average ash content of 35%. The washability characteristics of Indian coals are also poor, as coal mostly contains near-gravity material and the inorganic mineral matter is finely dispersed in organic matter of these coals (Meshram et al. 2015; Sharma and Dhawan 2018).

1.1 Background of the study

Physical beneficiation techniques such as dry fluidization, jigging, dense media/heavy media separations, hydroclone washings, magnetic separations, oil agglomerations, float and sink, air-dense medium separations etc. can remove ash from Indian coals but to a limited extent as described before (Rahman et al. 2017). These coal coals contain near-gravity material besides fine dissemination in organic matter. Thus, these processes have their limitations. The coal must be pulverised to effectively support the action of water, air, pressure or any magnetic separating device. The selective separation and incomplete removal of mineral matter make these processes ineffective, with poor liberation yields. The coal obtained could also be extensively

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dried for its maximum effective utilization to retain its calorific value. The need to reduce ash in coal is more apparent because there are several disadvantages associated with its presence. Ash reduces the calorific value of coal and increases transportation costs. Moreover, silicates and aluminosilicates largely result in fouling, slagging and clinkering of the furnace, heaters, turbines and reactors, which ultimately corrode and erode the equipment, thereby reducing its lifetime (Elliot 1981). Some volatile and extremely vulnerable toxic elements such as As, Se, Hg, B, and cyanates result in acute health issues when released into the atmosphere during coal combustion (Elliot 1981). The presence of certain metals such as Na and K, which, when present above the permissible limit, can act as an adhesive between the ash particles and thereby make the process of ash deposition on the boilers, reactors etc., much faster (Elliot 1981). These also unfavourably accelerate the combustion of coal. The removal of mineral matter is also important for recovering and recycling costly catalysts after the coal conversion reactions of liquefaction, gasification, depolymerisation or derivatisation, etc.

Therefore, removing the inorganic mineral matter from coal is essential to avoid the numerous problems caused by a large amount of ash in coal. This is crucial for the cleaner use of coal and would reduce the problems of handling coal as a chemical material in coal conversion and utilisation in industries. The super clean coal would make it a cleaner chemical raw material to provide a wide range of smart chemicals and materials, including nanocomposites and nanomaterials (Mathur et al. 2007; Dosodia et al. 2009).

In one of the techniques, the organic matter is extracted from the coal through solvent extraction using organic solvents, leaving behind ash-rich residual coal (Pande and Sharma 2002; Deonarine 2015). In another technique, the inorganic mineral matter is removed from the coal by chemical leaching using inorganic chemicals. The solvent extraction technique, i.e., organo-refining of coals, can afford the recovery of almost zero ash coal as super clean coal, leaving behind residual coal rich in mineral matter (Pande and Sharma 2002). The extractability of coals in organic solvents under milder ambient pressure conditions is usually less than 25%–30% (Sharma and Dhawan 2018). Extraction yields can be enhanced by higher pressure at elevated temperatures (Okuyama et al. 2004). However, this leads to changes in the organic chemical structure of coals. Moreover, operating under higher pressures and elevated temperatures is not convenient in industries that involve several unit operation problems besides safety issues. Moreover, higher extraction yields lead to the filtration problems of thicker coal slurries. Thus, removing mineral matter from coal should form an integral part of coal utilization, and options must be explored for chemical cleaning when the physical beneficiation processes remain ineffective.

Almost all the elements present in the periodic table are present in coals. Coal ash is primarily composed of silicates, aluminosilicates, iron oxides with variants of other oxides, such as those of calcium, magnesium, sodium, potassium, titanium etc., which form the major constituents. The other minor elements or trace elements present are strontium, nickel, zinc, cadmium, mercury, lead, antimony, uranium, chromium, vanadium etc. (Deonarine 2015).

To achieve maximum reduction in inorganic matter, chemical cleaning processes are used. This may also result in the deep cleaning of coals by removing a large portion of ash, which is ordinarily impossible by physical beneficiation techniques. Advanced techniques of beneficiation of coals have been reviewed by Meshram et al. (2015). Some coals with only exterior ash would show good liberation by physical beneficiation techniques, whereas chemical processes may have to be employed for others. It is essential to clean coals by removing undesirable and non-combustible inorganic mineral matter from coal for efficient use of coal. Two techniques of separation engineering can be employed to clean the coal. One obvious advantage of chemical leaching of coals over solvent extraction, i.e. organo-refining of coal, could be that here, the yields of clean coal are much higher than those from the organo-refining of coals, especially under atmospheric pressure conditions. Moreover, inorganic minerals separated from coals can lead to the recovery of value-added minerals.

1.2 Recovery of rare earth elements (Realms), lithium, aluminium, gallium silicon, titanium etc. from the mineral matter of coal: an extended application

Dodbita and Fujita (2023) have recently reviewed the research work on recovering rare earth elements from coal ash. The presence of realms in Indian coals has been reported earlier (Sharma and Dhawan 2018; Bhatia 2007). Almost all the elements included in the Periodic table are present in coals. Present authors feel that acid leachate (Sharma and Gihar 1991; Sharma and Singh 1995; Speight 2012; Dhawan and Sharma 2019) can be a potential source of the elements which are either being depleted fast and especially of those elements are in great demand but are scarcely available on earth. These could be Al, Ga, Ti and Ge and important and costly Realms. There is also a shortage of Li metal, which is vital for Li-ion storage batteries, which is significantly in demand for the storage of power generated by solar and wind renewable energy sources. There are limited Li mines in the world. Therefore, there is an obvious need for searching alternate sources of this metal Qin et al. (2015) have reviewed the potential of coal as a source of Li metal. Li et al. (2020) have also reported that coal leachates can be a good source of Li and Al. The use of organic carboxylic acids in recovering Realms from coal ash has been reported (Homa et al. 2023; Banerjee et al. 2023). Using inorganic acids, which are much more vital for the recovery of Realms from the coal ash, would be much better. Hence, the research on the chemical leaching of coals using inorganic acids such as HCL and HF is very obvious. Since minerals are already in the acidic extract in the acid leachate of coal, it would be economically more attractive to recover these from these leachates.

Organo-refining technology of coal also enhances the beneficiation and chemical leaching of coals; therefore, there is also a good scope for employing the integrated organo-refining and chemical leaching of coals (Giri and Sharma 2004; Dhawan 2019) for the recovery of valuable elements from coals. Detailed discussion on the same is beyond the scope of discussion presently.

Chemical leaching of coal Therefore, chemical leaching of coals using inorganic chemicals is a better option for cleaning the coals to obtain low ash cleaner coals. Chemical leaching involves the treatment of coals with inorganic acids and alkalis to reduce the ash and sulfur contents in coals. The most common reagents are NaOH, Na_2CO_3, CaO, $Ca(OH)_2$, lime, KOH, and mineral acids such as HCl, HF, HNO_3, H_2SO_4, HI. (Dhawan and Sharma 2019). Oxidizing agents such as H_2O_2, $Fe_2\ (SO_4)_3$, $K_2Cr_2O_7$, NaOCl, have also been used by some researchers. Mild leachants such as EDTA, citric acids, pyroligneous acids have also been used. The use of oxidising agents in acids has also been attempted. And this leads to the removal of pyritic sulfur. The reduction in mineral matter through chemical leaching of coals is defined by its degree of demineralisation (DoDe). The degree of demineralisation (%) is calculated as follows:

$$\text{Degree of demineralisation (\%)} = \frac{\text{Ash (feed coal)} - \text{Ash (leached coal)}}{\text{Ash (feed coal)}} \times 100\,\% \quad (1)$$

The first and easiest washing performed is the water washing of coals. This would dissolve all the water-soluble and vulnerable salts present as exterior components. Ammonium acetate has also been used to attack the ion-exchangeable cations generally present as carbonates in coals (Wijaya and Zhang 2011). Most coal minerals are solubilised in acids, generally at low pH. Therefore, single-step washings have been employed to remove the ash and sulfur in coals using these acids to the maximum extent possible. Steel et al. reported (Steel and Patrick 2001) that HCl can solubilise almost all minerals such as phosphates, carbonates and sulfates, which are primarily associated with significant elements such as Ca, Mg, Fe, Al, K, and Ti; however, this fails to dissolve silicates, some aluminosilicates and pyrites in coal. Thus HF (Steel and Patrick 2001 and 2003) was proposed to be an effective acid to solubilise almost all minerals present in coal, but it still failed to remove pyrites. Therefore, subsequent treatments with HCl followed by HF were proposed to remove almost all the minerals. However, for pyrite removal, Steel and Patrick (Steel and Patrick 2003) used HNO_3, the action of nitric acid mainly proved effective when used above a specific concentration.

In one of the techniques demonstrated on the single acid treatment of coal, the use of hydroiodic acid at 260 °C and 60 bar pressure on one of the Spanish coals could successfully altogether remove firstly inorganic sulfur in the first 10 min and then 70% of the organic sulfur in the next 10 min of the acid treatment (Andreas et al. 1996). Acidic ferric sulfate solution has also been used for the removal of pyritic sulfur, and this is commonly termed the Meyers Process (Meyers 1996) Bilgin et al. (2021) have recently used boric acid produced from boric minerals for the chemical leaching of coal with around 30%–40% removal of sulfur and ash from the coals.

1.3 Stepwise sequential alkali–acid leaching

Two-stage leaching becomes necessary because of the inability of one acid to remove the inorganic matter from coals altogether. The partial ability of these acids to selectively act upon the minerals sometimes requires using multiple acids on coal too. Steel et al. (2001a, b); Steel and Patrick (2003) have studied the action of HF leaching followed by HCl treatment on Australian Black coals at varying concentrations and times. The resulting product showed less than 1% ash and even as low as even 0% ash contents in treated coals. The collective action of HF on the silicates and aluminosilicates and the ability of HCl to act on Ca, Mg, Fe, Na, Al and Ti, primarily as carbonates and phosphates, could drastically reduce the mineral matter concentration in these coals. Steel and Patrick (2004) have also reported the recovery of HF after the HF leaching of coals. However, this involved several cycles of reaction steps.

There is a broad scope of using super acids and super bases in the chemical leaching of coals (Olah et al. 2009; Srivastava and Misra 2015). Some reactive ionic liquids may also be used to demineralise the coals. Lime and carbonic acid (from the CO_2) seem to be the cheaper chemicals; however, there may be a need to use elevated temperature and high-pressure conditions to carry out effective demineralisation. The use of alkalis such as NaOH or KOH has been made to leach the coals. The reaction of alkalis with silicates or aluminosilicates results in sodium silicate or sodium aluminosilicates. Research on alkali–acid leaching of Indian coals (Behera et al. 2018) has been conducted under milder ambient pressure conditions.

Earlier studies from the author's laboratory also involved using two-step alkali–acid leaching of coal where 74% degree of demineralisation could be obtained. Chemical reaction engineering studies were reported, including process kinetics and intensification studies (Sharma and Gihar 1991; Sharma and Singh 1995). Nabeel et al. (2009) used low concentrations of alkali and acid in the leaching process. A comparison of the degree of demineralisation by using aq. NaOH alone and HCl or H_2SO_4 treatments have also been reported. The use of lime in place of NaOH was also made. Some of the Indian coals have higher ash contents (>45%), and the inorganic mineral matter of some of these coals was found to show lesser reactivity towards aq. NaOH under milder ambient pressure conditions. With some Indian coals, the treatment with aq. NaOH at higher temperatures led to the formation of sodium silicate salts having varied leaching tendencies with HCl or H_2SO_4. This happened mainly when elevated temperatures under higher pressures were used to leach some Indian coals. Some low-rank coals, such as lignite or brown coals, are soluble in aq. NaOH and aq. KOH solutions even under milder conditions. Therefore, it would be challenging to demineralise such low-rank coals through alkali–acid leaching. Dhawan and Sharma (2019) have reviewed the research on advances in the chemical leaching, bioleaching and biodesulfurisation of coals.

It aimed to extend further studies on coals' stepwise successive sequential alkali–acid leaching. It was proposed to study the application of this technique to leach Indian coals having complex moderate to high mineral matter contents. Comparing the alkali–acid leaching with HF leaching for coals was also interesting. The studies were also extended to carry out HF leaching of the cleaner coal obtained from the alkali–acid treatment to obtain further demineralisation of coal. The effect of alkali–acid leaching on the solvent extraction of coal and vice versa forms a complete comparative study of the present discussion.

2 Experimental

Twenty Indian coal samples – Neemcha, Kedla, Pandra ECL, Giddi A, Bahula ECL, Tarmi, Sheetalpur ECL, Bachra CCL, Madhaipur, Parasea pit, Manderboni, Kendra, Belbaid, Phularitand, Sendra, Jeenagora, Bhagabandh, Moonidih, Bina and Neyveli lignite were procured from NTPC power station, New Delhi and Ministry of coal, Govt. Of India for solvent extraction studies. The coal samples were ground to − 60 + 120 BSS (British standard sieve), dried overnight at 105 °C and stored in desiccators. The proximate analysis and DoDe are mentioned in Table 1.

Chemicals used for the alkali–acid leaching process were sodium hydroxide, hydrochloric acid, and hydrofluoric acid, which are commercially available laboratory grade. All the extractions were performed under ambient pressure conditions without using any inert atmosphere.

2.1 Stepwise sequential alkali–acid leaching process

The coal samples (2 g) were first treated with 50 mL 20% aq. NaOH solution by placing the coal and 20% aq. NaOH solution in a round bottom flask fitted with a reflux condenser under ambient pressure refluxing conditions. The refluxing was carried out for 2 h. After thermal treatment, the reaction mixture was cooled, filtered, washed with water and dried overnight in a preheated oven at around 95–100 °C (Sharma and Singh 1995).

Then, the dried coal was placed in the desiccator till the coal cooled at room temperature. This NaOH pretreated coal was again taken with 50 mL 10% HCl solution in a 250 mL round-bottomed flask fitted with reflux condenser. The solution was again refluxed for 2 h. The reaction mixture was cooled, filtered, washed with water and dried overnight in a preheated oven at around 95–100 °C (Sharma and Singh 1995). This residual coal obtained was then used for ash determination using a furnace. The degree of demineralisation was calculated using Eq. (1) mentioned earlier in the text. Table 1 shows the proximate analysis of coals and the HGI values of the coal samples. Table 1 shows the Degree of demineralisation (DoDe) of coal samples.

2.2 Combinations of acids and alkalis

Based on the degree of demineralization results obtained for all the samples, three coals- Neemcha (34.36% ash), Pandra (48.80% ash) and Madhaipur (9.70% ash) were chosen for further alkali–acid combinations treatment. The same procedure as described above was adopted subsequently. Coal (2 g), HCl (10%) were taken in a round-bottomed flask (250 mL) fitted with a reflux condenser and refluxed under ambient pressure conditions for about 2 h. This was followed by the above-mentioned procedure to obtain the residual coal. This residual coal was then treated with 10% HF solution in a 500 mL plastic beaker with continuous stirring under ambient pressure room temperature conditions. This residual coal was then used for a degree of demineralization determination. This combination was also used for the demineralization of Pandra and Madhaipur coal.

Similarly, Neemcha, Pandra and Madhaipur coals were treated for just single acid treatment with 10% HF solution, and the resulting degree of demineralisation was noted due to just 10% HF treatment. A third combination where coal treatment with 20% NaOH solution followed by 10% HCl treatment, and then a third step where this residual coal was

Table 1 Proximate analysis and HGI values of the coal samples in the study area (NC-Non coking coal, C-Coking coal, SC-Semi-coking Coal)

Coal	Coal type	Ash (%, as received basis)	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	HGI	DoDe (%)
Sheetalpur ECL(NC)	Sub-bituminous	32.30	1.01	17.24	49.45	58.20	26.0
Bahula ECL(NC)	Sub-bituminous	32.90	1.70	26.12	39.28	60.54	55.9
Neemcha (NC)	Sub-bituminous	34.36	0.73	19.71	45.26	58.11	50.9
Tarmi (NC)	Sub-bituminous	38.50	1.00	27.85	32.65	62.41	21.6
Bachra CCL (NC)	Sub-bituminous	39.80	0.99	16.38	42.83	55.16	41.1
Giddi A(NC)	Sub-bituminous	43.60	1.12	18.18	37.10	53.75	28.9
Kedla(NC)	Sub-bituminous	44.80	0.99	17.18	37.03	52.32	52.6
Pandra ECL(NC)	Sub-bituminous	48.80	1.30	15.39	34.51	51.45	30.2
Madhaipur(C)	Sub-bituminous	9.70	6.90	40.34	43.06	71.40	15.7
Parsea Pit(C)	Sub-bituminous	12.70	1.90	39.88	45.52	68.45	13.3
Manderboni(C)	Sub-bituminous	13.89	7.40	37.13	41.48	72.43	15.3
Kendra (NC)	Sub-bituminous	26.27	3.80	32.32	37.61	55.67	51.6
Belbaid Colliery(SC)	Sub-bituminous	15.30	3.60	39.42	41.68	66.23	62.8
Phularitand(NC)	Sub-bituminous	45.30	0.20	18.60	35.90	52.43	19.9
Sendra(NC)	Sub-bituminous	36.50	0.20	17.50	45.80	55.86	54.6
Jeenagora(NC)	Sub-bituminous	26.10	0.10	22.40	51.40	57.23	56.6
Bhagabandh(C)	Sub-bituminous	13.30	0.04	31.30	55.40	70.61	57.8
Moonidih(C)	Sub-bituminous	15.60	0.40	25.20	58.80	69.49	22.5
Neyveli lignite(NC)	Lignite	5.20	9.10	58.00	27.70	–	–
Bina(NC)	Sub-bituminous	16.40	2.30	31.50	49.80	56.36	73.3

treated with 10% HF treatment was carried out for Neemcha, Pandra and Madhaipur coals. The degree of demineralisation for each of the three coals was then determined.

3 Results and discussion

3.1 Effect of time, temperature and HF concentration on the leaching of mineral matter from coals

Neemcha coal (2 g) was taken in a round-bottomed flask fitted with the reflux condenser and 20% aq. NaOH, then 10% HCl and then 10% HF for the varying lengths of time 1 h, 2 h, 4 h, 8 h and the extractability in each case was determined. Neemcha coal (2 g) was taken in a round-bottomed flask fitted with the reflux condenser and 20% aq. NaOH and then 10% HCl and 10% HF and the mixture was leached for 2 h under refluxing conditions and separately under room temperature stirring needs to see the effect of temperature on the extractability of the coal.

The optimisation of 20% aq. NaOH and 10% HCl have been reported from the author's laboratory before, but not the effect of HF concentration on leaching after the NaOH-HCl leaching. The leaching effect due to 0%, 2%, 5%, and 10% HF leaching was observed for the Neemcha coal. HF was treated by taking the coal in a plastic beaker and stirring it under room temperature conditions, as mentioned

Table 2 Effect of HF leaching on HCl-treated and alkali-acid-treated coals

Coal (% ash)	10% HCl	20% aq. NaOH and 10%HCl	10% HCl and 10%HF	10% HF	Alkali acid leaching (20% NaOH and 10% HCl) and 10% HF
Neemcha coal (34.36)	18.94	50.9	88.85	79.68	89.98
Pandra coal (48.8)	15.98	30.2	75.99	82.60	74.13
Madhaipur coal (9.7)	12.4	62.37	92.68	93.04	96.80

Maximum DoDe: Alkali–acid leaching followed by 10% HF treatment that led to maximum removal of the mineral matter from coals

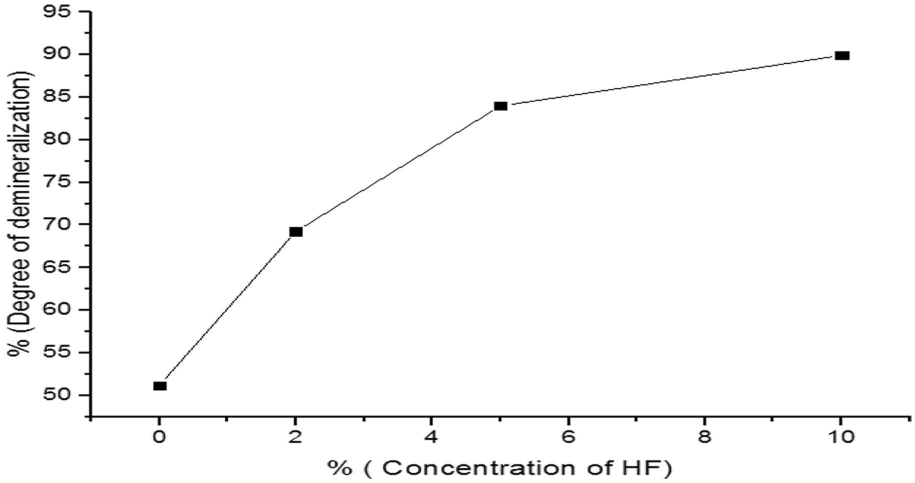

Fig. 1 Effect of HF concentration

in the procedure. The effect of HF leaching of HCl-treated and alkali–acid-treated coal samples is shown in Table 2. The effect of HF concentration is shown in Fig. 1. The effects of time and temperature are shown in Tables 3 and 4, respectively.

Effect of time

Table 3 Effect of time on the DoDe of NaOH-HCl-HF leaching of Neemcha coal

Coal	Alkali-acid leaching and 10% HF (1 h)	Alkali-acid leaching and 10% HF (2 h)	Alkali-acid leaching and 10% HF (4 h)	Alkali-acid leaching and 10% HF (8 h)
Neemcha	56.40	89.98	97.14	98.25

Effect of temperature

Table 4 Effect of temperature on the Dode of NaOH-HCl-HF leaching of Neemcha coal

Coal	Alkali acid leaching and 10% HF (2 h, R.T.)	Alkali acid leaching and 10% HF (2 h, Refluxion)
Neemcha	68.60	89.98

3.2 Stepwise alkali–acid leaching process

The stepwise alkali–acid leaching process involved the treatment of the coal (Neemcha) with 10% NaOH solution followed for 2 h, followed by obtaining the residual coal with the procedure mentioned before. The residual coal was then treated with 10% HCl solution for 2 h, followed by the same procedure to obtain the residual coal. This residual coal was then used to determine the degree of demineralisation.

This residual coal was obtained in the first step using 10% NaOH, and 10% HCl treatment was then used for the second step to obtain residual coal. In the second step, this residual coal was taken in a round-bottomed flask with 10% NaOH solution and refluxed for 2 h under ambient pressure conditions. Then, the mixture was filtered and dried as mentioned before in the procedure. This coal was again used for the 10% HCl treatment in a round-bottomed flask fitted with a reflux condenser for about 2 h. Then, the coal obtained was used to determine the final degree of demineralisation.

3.3 Organo-refining followed by alkali–acid leaching treatment and vice-a-versa

This process involves the stepwise combination of solvent extraction and alkali–acid leaching processes. The coal sample—Neemcha coal (2 g) was taken in a 250 mL round-bottomed flask fitted with a reflux condenser containing solvent (34 mL) and co-solvent (2 mL). The coal: solvent ratio of 1:17 (wt/vol; g/mL) and coal: co-solvent ratio of 1:1(wt/vol; g/mL) were used for the extraction and refluxed for 2 h and then filtered using a Whatman filter paper. After filtration, the residual coal (RC) was washed to remove the solvent, and RC was dried overnight at about 105 °C. The coal's weight loss was recorded to calculate the extraction yield. The extract obtained was distilled to remove the excess solvent, and the clean coal was recovered using water as the anti-solvent. The super clean coal (SCC) was dried overnight and weighed to calculate the extraction yield (Pande and Sharma 2002).

Residual coal obtained in this solvent extraction process was treated with 20% NaOH and 10% HCl solution, as mentioned in the procedure. The final residual coal obtained after solvent extraction and alkali–acid leaching treatment was then used to determine the ash contents and the degree of demineralisation concerning the ash contents after organo-refining (solvent extraction) and the starting raw coal used.

The same procedure was adopted simultaneously for the alkali–acid leaching, followed by the organo-refining procedure. After 20% NaOH–10% HCl treatment, the residual coal was used for the organo-refining process. Then the final degree of demineralisation was determined for the coal. The two processes were then compared for the coal treatment.

3.4 Degree of demineralisation (DoDe) of Indian coals through stepwise sequential successive (SST) alkali–acid leaching

Twenty Indian coals were subjected to subsequent sequential stepwise alkali–acid leaching using 20% aq.NaOH treatment followed by 10% HCl treatment. Table 1 shows the proximate analysis and HGI values of coal type of 20 Indian coals used in the present studies.

Mineral contents of some of the Indian coals were reported earlier (Dhawan et al. 2018; Dhawan and Sharma 2019). Indian coals have complex characteristics of ash, as has also been reported by Saikia et al. (2013). These authors have suggested that most alkali metals are aluminosilicates, and phosphates are a complex mixture of aluminosilicate salts. Thus, alkalis could react with aluminosilicates for leaching these ash constituents mainly. Sahoo and Sahu (2020) have also reported the mineral contents of fly ash of Indian coals.

Presently Indian non-coking and coking coals having wide-ranging ash contents from 9.7% to 48.8% were used for the studies. The highest DoDe was shown by Bina coal (16.4% ash), with almost 73.3% DoDe (Table 1). No specific trend of DoDe relating to the ash contents of the 20 Indian coals was observed. Of the 20 coals studied, nine coals showed more than 50% DoDe, whereas 8 coals showed less than 30% DoDe. Surprisingly, some low ash coals showed less than 20% DoDe. This showed that the nature of the inorganic mineral matter, especially its reactivity towards alkali and acid used, was responsible for the low DoDe, i.e., reactive separation of coals. Therefore, further studies are required.

3.5 Possible mechanism of SST of alkali–acid leaching

Bhagabandh coal (13.3% ash) upon SST with 20% NaOH followed by 10% HCl treatment had shown almost 57.8% DoDe, Belbaid coal (15% ash) had shown 62.8%, DoDe, whereas Bahula ECL coal (32.9%ash) had shown 56%. Sendra coal (36.5% ash), Kedla (44.8% ash) and Neemcha (34.4% ash) gave almost 54.6%, 52.6% and 50.9% DoDe, respectively. Madhaipur (9.7% ash), Parasea Pit (12.7% ash), Manderboni (13.9% ash) showed just 15.7%, 13.3% and 15.3% of DoDe only. Thus, it was found that some of the low ash coals could not give good DoDe. This showed no correlation of mineral matter contents with the DoDe of coals through SST using alkali-acid. Thus, with such varied results, no specific trend of DoDe through SST using alkali and acid treatments could be derived for the wide variety of coal samples studied presently. Therefore, the type of mineral matter and its reactivity towards alkalis and acids was more critical. The lesser mineral matter may not make it more amenable to leaching. The association of organic matter with mineral matter may also be significant from the accessibility (mass transfer) point of view. However, this appeared to be of lesser concern as the coals used for the alkali-acid SST were in fine powder form (60–120 BSS mesh size). The type of interactions of these mineral matter components due to non-covalent interactions between the mineral matter and the organic matter in coals primarily play a role in their leaching characteristics. However, this aspect has been studied and discussed in the later part of the paper. This could also be due to the large number of sodium salts forming from the reaction between the silicates, and aluminosilicates present in the mineral matter in coals, which undergoes reaction with NaOH. According to one of the earlier reported works from the author's laboratory (Sharma and Singh 1995), it was also observed that the action of the alkali on the surface of the coal could break some of the covalent bonds, hydrogen bonds and weak Van der Waals forces present inside the cross-linked three-dimensional gel network macromolecular structure of coals. This results in the loosening of the solid coal constitution by breaking the non-covalent interactions between the organic and inorganic coal network. Progressive reactive separation of coals would expose more inorganic mineral matter for leaching action.

The formation of sodium silicates, sodium aluminosilicates, and pyrites during the treatment of sodium hydroxide with coal, followed by the HCl treatment, renders the dissolution of the quickly acid-soluble compounds (Steel and Patrick 2001). Steel and Patrick (2001) have reported that HCl dissolves almost all the minerals, such as carbonates, sulphates, and phosphates, which are mainly associated with some elements such as Ca, Mg, Fe, Al, K, Ti, but acid alone does not dissolve aluminosilicates, silicates, and certain pyrites however these are converted into their soluble form using initial treatment with NaOH solution. Thus, with conversion to sodium silicate and sodium aluminosilicate form, these are converted to acid-soluble forms, which can then be removed upon treatment with the acids and water.

The extent of the DoDe of these coals would largely depend upon the amount of the convertible mineral matter associated with coals (Sharma and Gihar 1991). Earlier studies from the authors and laboratory were also reported on the SST process's reaction kinetics and process intensification using alkali–acid leaching (Sharma and Singh 1995; Nabeel et al. 2009). The higher concentrations of alkalis and acids lead to an increase in the DoDe of coals. Nabeel et al. (2009) even used dilute alkali and acid solutions for the DoDe of some Indian coals and this work seemed to be of interest for the process economics of chemical leaching of coals. Coals having reactive mineral matter would be more suitable for this.

The following reactions take place during the NaOH treatment of coals.

$$\mathrm{SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O} \tag{2}$$

$$\mathrm{Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O} \tag{3}$$

The reactions for the recovery and reuse of alkali and acid used in the SST using alkali–acid leaching of coal was reported earlier (Sharma and Gihar 1991). Attempts were made to understand the reason for the lower DoDe in coals after considering the types of mineral matter present in these coals. The higher DoDe in the case of the Belbaid coal (62.8%) (Table 2) could be due to more reactive mineral matter components having loose non-covalent associations of the inorganic matter with the organic coal macromolecular network. Almost 99.6% reduction in the Al content and more than 90% reduction in most of the significant elements upon treatment with basic solvent ethylenediamine (EDA) could suffice the ability of a robust inorganic alkali to dissociate non-covalent interactions in Belbaid coal that may have resulted in such high degree of demineralisation as reported earlier (Dhawan et al. 2018; Dhawan and Sharma 2019). This might also be a possible reason for Kendra coal's high Dode (almost 52%) (Table 2). With just 16.6% ash, Bina coal gave nearly 73% DoDe. The possible reason could again be the chemical nature, i.e., the reactivity of the inorganic matter that could efficiently react with NaOH to form sodium silicates, sodium aluminates or sodium aluminosilicates, which on further treatment with acid would have been dissolved. In the case of Moonidih coal, having a low ash (almost 15.6% ash), the amount of DoDe achieved was only 22.5%. Attempts were made to understand the possible reason by determining the presence of significant elements. The presence of major elements such as Mg, Na, K, Ca in much lower amounts could be the reason for the lower reactivity towards the NaOH (Dhawan et al. 2018; Dhawan and Sharma 2019). Earlier studies from the authors laboratory reported (Dhawan et al. 2018; Dhawan and Sharma 2019) the analysis of mineral matter constituents in Indian coals. In the case of the Bhagabandh coal, the high concentration of the significant element Ca compared to the Moonidih coal would have resulted in a higher DoDe upon washing with the acid, resulting in almost 58% DoDe as compared to 22.5% in the case of Moonidih coal.

In the case of a very high ash Pandra coal (48.8% ash), the DoDe of 30.2%. could be achieved, which showed that the higher concentrations of Fe and Al (Dhawan et al. 2018; Dhawan and Sharma 2019) as compared to the other major and trace elements could be the reason for this. In this case, the pyrites present were not readily removable by the HCl treatment. The action of 20% NaOH solution could only partially react with aluminosilicates and silicates along with pyrites. The lignite being polar (with phenolic and carboxyl groups) was found to dissolve in the aq. NaOH solution. Further studies on the relation of the types of mineral matter with DoDe of coals through SST using alkali-acid are warranted.

Based on the DoDe results obtained presently, the following three coals: Neemcha coal (34.36% ash), Pandra coal (48.80% ash) and Madhaipur coal (9.70% ash), were chosen for further studies to maximise the DoDe. The ash contents and DoDe for these coals covered a wide range. DoDe through SST using 20% NaOH and 10% HCl leaching for these coals were found to be in the 30% to 60% content, i.e., Neemcha coal (51.2%), Pandra coal (30.2%) and Madhaipur coal (62.4%). Steel et al. (2001a, b) have reported the ability of HCl to solubilise the salts of Ca, Mg, Fe, Al, K, and Ti and its inability to solubilise the silicates, aluminosilicates and pyrites in the coal. Therefore, three coals were treated with 10% HCl to determine the amount of just HCl soluble components in the coals. These coals showed lower DoDe, i.e., Neemcha, coal (19%), Pandra coal (16%) and Madhaipur coal (12%). This showed that there is a presence of a low proportion of minerals which can be solubilised in the HCl. Thus, this also showed that the balance of the silicates, aluminosilicates and pyrites is higher in the overall mineral contents in these coals. Therefore, upon pretreatment with NaOH, when followed by the action of HCl, this resulted in increased DoDe in Pandra coal (30.2%), Neemcha coal (50.9%,) and Madhaipur (62.8%). This was more than the DoDe of 12% to 19% observed by the HCl treatment. Thus, this was due to the formation of sodium silicates, sodium aluminosilicates, and pyrites that were then solubilised by the HCl, resulting in the enhanced DoDe of these coals.

Steel et al. (2003) reported using HF in the leaching of the coals and reported good DoDEe of coals. HF can solubilise almost all minerals in coal except certain pyrites. Three presently selected Indian coals were subjected to leaching by using 10% HF under room temperature stirring conditions. Table 3 shows that Neemcha coal (79.6%), Pandra coal (82.6%) and Madhaipur coal (93%) showed good DoDe. However, as Steel et al. (2003) reported, certain minerals do not solubilise the HF. Therefore, it was decided to adopt the stepwise leaching approach using 10% HCl in the first step and then 10% HF in the second step. The DoDe observed by the use of the stepwise action of these two acids was found to be Neemcha coal (88.8%), Pandra coal (76%) and Madhaipur coal (92.7%) (Table 3), which showed that the stepwise action of 10% HCl–10% HF treatment removed good amounts of minerals from these coals, though still there are coals where the minerals which are not entirely removed by the stepwise action of HCl-HF acids.

Studies were further extended to investigate the effect of HF leaching of NaOH-HCl demineralised Neemcha, Pandra and Madhaipur coals. The combined result of the stepwise leaching using alkali-acid i.e. 20% aq. NaOH–10% HCl followed by the action of 10% HF led to the enhancement in the DoDe of Neemcha coal (75%), Pandra coal (89.9%) and Madhaipur coal (96.8%) (Table 3). The highest Dode was shown for the Madhaipur coal. These studies showed that the HF treatment led to further enhancement in DoDe of these coals after the SST of 20% aq. NaOH–10%HCl treatment.

However, a negligible effect of the HF treatment was seen in the high ash Pandra coal case, where the highest DoDe had been reached with a single HF treatment. Table 3 shows the results of the Dode observed through HCl treatment alone, HF treatment alone, stepwise HCL-HF treatments and stepwise NaOH-HCL treatments followed by HF leaching of Neemcha, Pandra and Madhaipur coals. HCl treatment alone showed poor DoDe of these coals (Table 3). HF leaching showed higher DoDe of these coals. Stepwise HCl-HF treatments led to the enhancement of the DoDe of this coal. However, HF leaching alone was also found to be a good option. The stepwise NaOH-HCl treatment followed by HF leaching of coals showed the higher DoDe of Pandra coal (75%), Neemcha coal (89.9%), and Madhaipur coal (96.8%). HF treatment led to the further leaching of coals, showing the increase in the DoDe of alkali-acid treatment of coals in 2 coals, whereas in one case, it did not show any effect. Thus, this showed that the chemical leaching depends on the type of mineral constituents present in coals. The reactivity of mineral matter constituents with the leaching agents is essential.

3.6 Process intensification studies of the SST of alkali–acid leaching and 10% HF treatment

The effect of various parameters, such as the time for the SST (using alkali-acid) and then followed by 10% HF leaching, temperature, and concentration of HF on DoDe of coal, was studied using Neemcha coal (34% ash). This coal was selected for the study as this had nearly the average ash content amongst the coals studied presently. This had shown a reasonable DoDe (> 50%) through the SST using 20% NaOH–10% HCl for the chemical leaching.

Effect of time: The treatment time was fixed for 1 h using all the reagents, i.e., firstly 20% NaOH treatment and then 10% HCl treatment and then this was further followed by treatment with 10% HF (under the stirring conditions). These three treatment steps showed 56% demineralisation, almost 5% higher than that obtained by 2 h NaOH–HCl leaching. Therefore, HF positively enhances the deashing even if it is just for an hour of the room temperature stirring treatment (Table 4). With the subsequent increase of time to 2 h from 1 h in each NaOH, HCl and HF treatment, the demineralisation increased to about 90%. Thus, the reaction time affects the leaching through the NaOH treatment followed by washing with HCl and then HF treatment. These treatments greatly solubilised the minerals in the coal, resulting in a more significant enhancement in the DoDe of coal. When the time was further increased to 4 h, almost 97% demineralisation was observed, close to the exhaustive effect attained when further increased to 8 h. The DoDe of 98.2% could be achieved with 8 h of alkali–acid and 10%HF treatments. Further increase was not observed upon the addition in time.

Effect of temperature: The effect of temperature, i.e. refluxing and room temperature stirring, was shown by the treatment of the coal under both conditions for 2 h each with alkali (20% NaOH), acid (10% HCl) and 10% HF. At room temperature, almost 70% DoDe could be observed in this 3-step treatment. In contrast, SST using alkali–acid leaching under reflux conditions and HF treatment under room temperature conditions showed almost 90% DoDe. This indicates that temperature does play a role in enhancing the demineralisation of the coal where the thermal treatment improves the mass transfer effects by thermally mobilising the molecules. The reactions are mainly mass transfer controlled. As determined by the studies of the activation energy of the reaction between aluminosilicates and NaOH (Zeng and Li 2012). The area of contact under refluxing conditions increases, thereby increasing the demineralisation of the coal as compared to that under room temperature stirring conditions. The association of mineral matter with organic matter and its dispersion are also essential factors. The effect of the concentration of the alkali (20% NaOH) and 10% HCl leaching on the DoDe of coal has been reported earlier by the authors (Sharma and Singh 1995). Nabeel and Sharma (2009) used dilute alkali and acid concentrations for the chemical leaching of coals to economise the process. Depending upon the reactivity of the mineral matter present and the association of the mineral matter with the organic matter of coal, it may be possible to use dilute alkali and acid concentrations.

The effect of HF concentration after the treatment of the coal with alkali-acid has not been reported before. Upon increasing the concentration of HF from 2% to 5%, a subsequent increase in demineralisation was observed. An increase from 67% to 83% could be observed upon increased HF concentration (Fig. 1). Under the given room temperature stirring conditions, due to the corrosivity of the HF, a limit of 10% HF was set for the coal treatment. With the increase from 5% to 10% HF concentration, almost 90%

DoDe could be achieved. This showed that HF concentration greatly affected the demineralisation of the Neemcha coal after the alkali-acid treatment (Table 4). These studies are propitious for the further process development engineering studies of this process using fluidised bed conditions.

In this process, using a stepwise approach in the first step treatment of Neemcha coal with 10% aq. NaOH for 2 h and then 10% aq. HCl showed about DoDe of 54%. Then, the treated and demineralised coal obtained after this first treatment step was subjected further into the second step with 10% NaOH followed by 10% HCl leaching. This resulted in as high as 80% DoDe. This showed that more of the mineral matter was exposed after each treatment for the reactive separation. The alkali-acid leaching process is mass transfer controlled. During the repeated and cascaded treatments, more inorganic mineral matter is exposed and becomes available for reactive separations through subsequent treatments. As described before, Nabeel and Sharma (2009) also reported on the multi-step leaching of coals using very dilute alkali and acid concentrations, which may be more suitable for coals with reactive mineral matter.

To study the effect of alkali–acid time, The Neemcha coal was also subjected to the SST alkali-leaching for 4 h at each treatment step, i.e., a total treatment time of 8 h. This resulted in 38.9% of DoDe, much lower than the 80% of DoDe observed through the repeated cascaded multi-step alkali–acid treatment for the total 8 h. Therefore, the multi-step treatment showed more DoDe simultaneously, as observed in the case of single SST leaching using the alkali-acid leaching process. The possible reason could be the breaking of specific non-covalent interactions in coal due to the action of alkali and then the acid, which breaks specific other interactions such as the H-bonds, interactions between the mineral matter and the inorganic matter in coals. According to one of the previous studies (Nabeel and Sharma 2009), the alkali can diffuse inside the coal pores and react with the minerals present. The reaction occurs at the peripheral sites or the surface of coal particles. Thus, after the initial alkali and acid treatment, more surface gets exposed for about 2 h each. Therefore, this would increase the DoDe of coal.

To compare the effect of time, the treatment of the coal with 10% NaOH was extended for 6 h. This resulted in a DoDe of almost 59%. This showed that the cascaded multi-step SST treatments using alkali–acid was more beneficial for obtaining higher DoDe of coal doses. Each treatment step exposes more coal mineral matter for chemical treatments by enhancing the mass transfer. Though the stepwise approach may require more repeated operations, however, the DoDe obtained is higher; thus, a continuous process may be devised for the repeated SST of coals using alkali-acid. Fluidised reactors may be designed for this process. Further process engineering work may be undertaken on these lines.

It was also noted that the HF leaching of Neemcha coal after the alkali-acid leaching had shown much higher DoDe (80%) than that obtained by using two alkali-acid treatment steps, i.e., cascaded multi-step alkali-acid leaching process. This showed that HF leaching was better than the second repeated step of the alkali-acid leaching process. Steel and Patrick (2004) have reported on the recovery and recycling of HF after the leaching of coals to obtain ultra-clean coals. However, further work would be required to make the chemical leaching of coals cost-effective as it involves many steps.

3.7 Organo-refining followed by alkali-acid leaching of Giddi A coal

A parallel approach for the demineralisation of coal for producing cleaner coal is solvent extraction by using organic solvents wherein the almost ash-free organic matter is recovered from the coal as the super clean coal. However, this leaves behind residual coal richer in the inorganic mineral matter. Extensive research on the solvent extraction of coals to produce nearly zero ash super clean coal has been carried out in authors' laboratories in the past (Pande and Sharma 2002; Sharma and Dhawan 2018). This process was termed the organo-refining of coals. Presently, the Giddi A (non-coking bituminous) coal (43.7% ash) was subjected to organo-refining by using N-methyl pyrrolidone (NMP) containing a small amount of ethylenediamine (EDA) for 2 h. under reflux conditions at atmospheric pressure (Pande and Sharma 2001). Giddi A coal was chosen as this had shown just 29% DoDe through SST using alkali-acid. This resulted in almost 28% of coal recovery as the super clean coal (SCC) had 2% ash contents. The ash contents in the residual coal were found to be 56% compared to the 43.7% in the original coal. It was essential to demineralise the residual coal for its practical use as a cleaner fuel and feedstock.

Therefore, the residual coal obtained after the organo-refining process was subjected to SST using alkali-acid (20% aq. NaOH–10% HCl) leaching. its demineralisation. The demineralised residual coal showed an ash content 35.3%, and the DoDe shown was 53.9% against the 29% observed for the raw Giddi A coal. Removal of organic matter through the organo-refining process exposed more mineral matter for the reactive separation using an alkali-acid leaching process. The mineral and organic matter interactions may also have been let loose. Thus, due to the loosening of the association of mineral matter with the macromolecular network in coal, the reaction of these mineral constituents with NaOH increases. Therefore, more aluminosilicates and silicates could be converted to sodium silicates and sodium-aluminosilicates, which could have been removed with the subsequent acid washing. This super-clean coal can produce premium chemicals, carbon nanomaterials, and nano fuels. (Mathur et al. 2007; Dosodia et al. 2009; Sharma and

Dhawan 2018). The residual coal can also be demineralised by chemical leaching for other uses, including gasification. Research may be further extended to economise the processes of organo-refining and alkali-acid leaching of coals.

3.8 Alkali-acid leaching followed by Organo-refining of Giddi A coal

It was also decided to study the reverse approach, i.e., first employing the alkali-acid leaching using 20% aq. NaOH and 10% HCl, then subjecting the demineralised coal thus obtained to the organo-refining process. Almost 29% DoDe was obtained through alkali-acid leaching of the Giddi A coal. The ash content in the leached l coal was 35.3% against the 43.5% in the original Giddi A coal. The leached coal thus obtained was subjected to the organo-refining treatment by using NMP as a primary solvent with small contents of EDA as a cosolvent under reflux conditions under ambient pressure conditions for 2 h. About 36.8% of coal was rendered extractable as against the 25% extraction yield for the untreated Giddi A coal. This showed that the alkali-acid leaching was a beneficial treatment for enhancing the extractability of coal. However, the ash content in the residual coal obtained after the solvent extraction was found to be 42%, closer to the original coal's ash content. The extraction yield on the residual coal basis was found to be 35.2%, whereas on the SCC basis, this was found to be 36.8%.

The 12% increase in the extraction yield was due to removing inorganic mineral matter from the coal using alkali and acid. This treatment exposed more of the organic matter of coal for extraction. The diffusion of solvents inside the solid coal mass becomes easier by breaking specific interactions due to the alkali's and the acid's selective action on the mineral matter, compared to the raw coal. Another advantage of the alkali-acid leaching process would be that removing mineral matter from coal would conserve the solvent requirement for the organo-refining process. There is a broad scope for further studies in developing the integrated approach. This showed that by integrating the application of both these processes, the use of chemicals might be conserved over those used when these processes are employed separately. However, these integrated processes may need to be more economically attractive and further research would be required.

4 Conclusions

To increase the efficiency of the demineralisation process, various combinations of treatments, such as stepwise alkali–acid treatment followed by the HF treatments, were studied. NaOH–HCl leaching followed by HF leaching was the best for demineralising low to high-ash Indian coals having complexly associated mineral matter in coals. HF was more effective for demineralisation than the NaOH–HCl leaching process. However, HF is costly. Therefore, to reduce the amount of HF used and to take care of its recovery aspects, the alkali-acid combination (NaOH–HCl) followed by HF leaching was a better option from the process engineering point of view. Stepwise successive sequential leaching was found to increase the overall degree of demineralisation. Another approach where the integrated process of alkali-acid leaching followed by solvent extraction was studied using a high ash Indian coal, the alkali–acid pretreatment was found to enhance the recovery of super clean (having almost zero ash) by increasing extraction yield by 12%.

The acid leachates recovered after the chemical leaching processes can be used to recover precious metals such as lithium, aluminium, gallium silicon, and titanium. These also include much-desired and scarce rare earth metals such as Rh, Pd, Pt, Ir, Au etc. In fact, more important is the recovery of Li for the Li-ion batteries and rare earth metals required for several modern industries. The processes for recovering these premium metals from the coal ash have already been developed and can be utilized. Here, minerals are already present in the acidic extract. The acid leachates can also capture CO_2 to reduce the greenhouse effect and climate change. Processes for the same have also been already developed.

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Declarations

Competing interests The authors declare no competing financial interests in the article.

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