

Accepted Manuscript

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PII: S0301-7516(17)30048-0

DOI: doi: [10.1016/j.minpro.2017.02.013](https://doi.org/10.1016/j.minpro.2017.02.013)

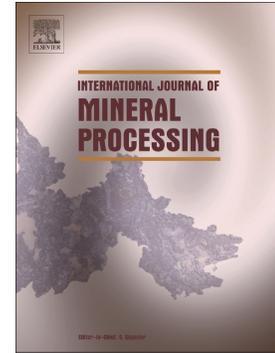
Reference: MINPRO 3024

To appear in: *International Journal of Mineral Processing*

Received date: 29 September 2015

Revised date: 17 February 2017

Accepted date: 20 February 2017



Please cite this article as: Wencheng Xia, Guangyuan Xie , A technological review of developments in chemical-related desulfurization of coal in the past decade. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Minpro(2017), doi: [10.1016/j.minpro.2017.02.013](https://doi.org/10.1016/j.minpro.2017.02.013)

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A technological review of developments in chemical-related desulfurization of coal in the past decade

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Abstract: Coal desulfurization prior to combustion, coking or gasification is benefit for both the upgrading of quality of commercial coal and the protection of the environment. The sulfur in coking coals usually makes coke unqualified while that in power coals creates several environmental problems, such as acid rain and air pollution. The sulfur forms in coal are primarily divided into two types, i.e. inorganic sulfur and organic sulfur. In most cases, inorganic sulfur is relatively easier to remove than organic sulfur by gravity separation after liberation pretreatments. The primary desulfurization methods include physical, physico-chemical, chemical, and microbial desulfurization. Among the above-mentioned desulfurization methods, chemical-related desulfurization is considered to be the most effective methods for both inorganic and organic sulfur, which is essential to be reviewed. This review is to highlight the developments in coal chemical-related desulfurization, including acid/alkaline leaching, H₂O₂ oxidation, electrochemical reduction, solvent extraction, pyrolysis, air oxidation, microwave/ultrasonic assisted desulfurization in the past

decade. The effective and future desulfurization technologies are recommended throughout this review.

Keywords: Coal desulfurization; acid leaching; alkaline leaching; oxidation; microwave; ultrasonic

1. Introduction

The main uses of coal are to produce coke for iron smelting, or to generate power for social development, or even to provide raw materials for industrial applications. Prior to its use (combustion, coking or gasification), demineralization and desulfurization are required to meet the quality of commercial coal as well as reduce the environmental pollution (Meshram *et al.*, 2015). Even though the desulfurization process in coal-fired units has been well developed based on flue gas desulfurization technologies, the desulfurization of coal prior to combustion is still considered to be the most effective and economic methods for ensuring the clean and environmentally friendly use of coal (Meyers *et al.*, 1972 Pietrzak *et al.*, 2007 Pietrzak *et al.*, 2006).

Nowadays, coal is primarily cleaned in coal preparation plants. The primary cleaning methods in coal preparation plants are gravity separation and flotation. Gravity separation is achieved by using the difference in gravity between coal and gangue particles whereas flotation is based on the difference in the surface hydrophobicity between coal and gangue (Aydin *et al.*, 1996). However, gravity separation and flotation have little effect on the removal of organic sulfur. In addition, a lot of inorganic sulfur is also difficult to remove while the disseminated grain size of inorganic sulfur is very fine. The inorganic sulfur, such as pyrite is usually associated

in the organic materials of coal, which makes inorganic sulfur difficult to remove using single gravity separation. Meanwhile, the floatability of fine inorganic sulfur minerals is similar (in a certain respect or degree) to that of coal particles, and hence the difference in the floatability between inorganic sulfur and coal materials is small (Ayhan, 2009). As a result, it is difficult to achieve an effective removal of fine inorganic sulfur minerals using single flotation.

Because inorganic sulfur, such as pyrite is commonly associated with gangue particles, the demineralization and cleaning processes of coal not only remove the ash minerals in clean coal but also reduce the clean coal sulfur content (Howard *et al.*, 1977). However, organic sulfur is associated with organic materials, which determines the difficulty in removing organic sulfur from clean coal.

In China, the allowed sulfur content in clean coal is usually below 1%. There are many sulfur-rich coal mines in southern China, and the sulfur content of clean coal is usually more than 1% while the sulfur forms in sulfur-rich coal in southern of China are primarily made up of organic sulfur. Hence, coal desulfurization is especially important to qualify the clean coal for organic sulfur-rich coals (Braden *et al.*, 2001 Pietrzak *et al.*, 2003 Pietrzak *et al.*, 2004).

The desulfurization methods include physical, physico-chemical, chemical, microwave/ultrasonic assisted and microbial desulfurization. Physical and physico-chemical methods include gravity and magnetic separation, flotation, oil agglomeration. There are sometimes effective and economic desulfurization technology for coals with high inorganic sulfur content while the inorganic sulfur in

raw coal is coarse grained disseminated. However, they are powerless while inorganic sulfur in raw coal is fine grained disseminated as well as the main sulfur consists of organic sulfur (Xia *et al.*, 2015). Microbial desulfurization is an environment friendly method in the desulfurization of coal, but it is still difficult to find out the effective funguses to save the biodesulfurization time (Rossi, 2013 Chandra *et al.*, 1988). Microbial desulfurization will be developed quickly in the future since the environmental problems are attracting the people's attention more and more (Ghosh *et al.*, 2013 Ghosh *et al.*, 2015).

Therefore, chemical desulfurization is usually considered to be the most effective methods for both inorganic and organic sulfur, which is essential to be reviewed. As shown in **Figure 1**, this review is to highlight the developments in coal chemical-related desulfurization, including acid/alkaline leaching, H₂O₂ oxidation, electrochemical reduction, solvent extraction, pyrolysis, air oxidation, microwave/ultrasonic assisted in the past decade. The chemical-related reagents assisted desulfurization technologies are research hotspots while the thermal/oxidation and physical energy assisted ones are considered as the new research fields in coal desulfurization. These two aspects can be combined and organized to achieve a better and further progress into coal desulfurization.

2. Literature review

2.1. Acid leaching

Acid leaching method changes the forms of sulfur in coal and hence is considered effective for the desulfurization of both inorganic sulfur and organic

sulfur.

Vaccaro (Vaccaro, 2010) found HF aqueous solution treatment on coal samples could reduce mineral matters of coal samples. Guru (Gürü, 2007) used nitric acid solution to oxidize combustible sulfur in the coal into sulfate form in the ash, and the maximum desulfurization efficiency was 38.7% of the original combustible sulfur after nitric acid solution treatment.

Alam et al. (Alam *et al.*, 2009) used HNO₃/HCl leaching method to further remove the sulfur from Tabas Mezino coal concentrate from froth flotation because froth flotation could not remove the total sulfur effectively. Therefore, HNO₃/HCl leaching was combined with flotation for the desulfurization processes. It was found that nitric acid was much more effective than HCl. The combination of flotation and acid leaching is a remarkable and effective choice for the desulfurization of Mezino coal.

In another study, the combination method was also used by Davalos et al. (Davalos *et al.*, 2009). They used a combination of sulfuric acid and hydrogen peroxide as oxidant to remove pyrite from coal. As shown in **Figure 2**, the primary chemical reaction is the elimination of pyrite, and the preferential release of iron produces a layer of "polysulfide" or "metal deficient" on pyrite surface. Mukherjee and Srivastava (Mukherjee *et al.*, 2004) also found that using a combination of hydrogen peroxide and dilute sulfuric showed better desulfurization and demineralization performance of high-sulfur northeastern India coal than that using hydrogen peroxide alone. Almost complete sulfate and pyritic sulfur are removed by

using hydrogen peroxide solution.

For the mechanism study, Borah et al. (Borah *et al.*, 2001 Borah *et al.*, 2005) indicated that organic sulfur, especially for aliphatic sulfur compounds could be oxidized using peroxyacetic acid. They also investigated the effect of six metal ions (Cu^+ , Ni^{2+} , Co^{2+} , Sn^{2+} , Pd^{2+} and Sb^{3+}) on coal desulfurization and found that the lowest sulfur loss with Ni^{2+} ion whereas the highest desulfurization with Pd^{2+} ion were observed.

2.2. Alkaline leaching

Mursito et al. (Mursito *et al.*, 2011) added alkaline into a laboratory-scale 0.5 L batch reactor in order to enhance the hydrothermal treatment of high-sulfur coal from Banten, Java-Indonesia. The total sulfur content was reduced from 3.1 to 1.7 % by hydrothermal processing without the addition of NaOH during the desulfurization process. However, after the addition of NaOH concentration of 0.025 mol/g, the total sulfur content was reduced from 3.1 to 0.3 %, which showed a 90% reduction in the total sulfur content.

Since flotation cannot remove organic sulfur effectively, froth concentrate can be leached using aqueous NaOH for a further desulfurization. It was found that the total sulfur of Hazro (Turkey) coal was reduced by 88.06% using a combination of froth flotation and sodium hydroxide leaching methods (SAYDUT *et al.*, 2007). Abdollahy et al. (Abdollahy *et al.*, 2006) also found that both organic and inorganic sulfur in mezino coal could be effectively removed using a combination of flotation and potassium hydroxide/methanol leaching methods.

Li and Cho (Li *et al.*, 2005) found that more than 70% of pyritic sulfur in Pittsburgh No. 8 coal was removed at the conditions of 0.4 M hypochlorite, 0.4 M NaOH, and 90 °C. The 37.8% of organic sulfur in Illinois No. 6 coal was removed at the conditions of 0.4 M hypochlorite with room temperature, followed by hydrolysis at 0.3 M NaOH and 90 °C. Charutawai et al. (Charutawai *et al.*, 2003) investigated the supercritical desulfurization of Mae Moh (northern Thailand) coal with ethanol/potassium hydroxide in a semi-continuous reactor and found that the temperature and KOH concentration had significant effects on the reduction of pyritic sulfur and total sulfur. In another study, Ratanakandilok et al. used a combination of methanol and KOH to improve the desulfurization process. Both inorganic and organic sulfur were removed effectively. The addition of KOH in the methanol solution could obviously improve the sulfur removal from Mae Moh coal (Ratanakandilok *et al.*, 2001).

In some cases, a combination of alkali and acid treatment was also needed in coal desulfurization process. Mukherjee (Mukherjee, 2003) used a mixture (1:1) of 16% sodium hydroxide and potassium hydroxide solution to treat Assam coal firstly, and then used 10% hydrochloric acid to treat the treated coal. As result, about 50-54% of inorganic sulfur and around 25% of organic sulfur were removed. Demirbas (Demirbaş, 2002a) used the water-soluble fraction of biomass ash to produce an aqueous alkaline solution for the alkaline desulfurization of both pyritic and organic sulfur for Turkish lignite. The pyritic sulfur was proved to be effectively removed using biomass ash (Demirbaş, 2002b).

In another study, the removal of mineral matter in coal (Tata Steel Company) was achieved by aqueous alkali leaching at elevated temperature, followed by acid washing. The ash content of coal could be reduced by more than 50% using this method (Dash *et al.*, 2013). Purohit *et al.* (Purohit *et al.*, 2014) successfully used a two-stage leaching process i.e. alkali leaching followed by acid leaching to further reduce the ash content of gravity-separated concentrate of Hingula coal.

It is also proved that the alkali leaching followed by acid washing treatments not only reduce the coal sulfur content but also remove the coal ash content.

2.3. H₂O₂ oxidation

Hydrogen peroxide acts as an oxidizing agent during the desulfurization process. The H₂O₂ concentrate, temperature, and treatment time usually have significant effects on the desulfurization process of coal (Nam *et al.*, 2004a). Guru *et al.* (Gürü *et al.*, 2008) concluded that combustible sulfur in Tufanbeyli coal could be converted to non-combustible sulfate form in the ash during the oxidation processes with hydrogen peroxide solution.

Baruah and Khare (Baruah *et al.*, 2007) used an oxidative medium (combining H₂O₂ and HCOOH) to remove about 84% of inorganic sulfur and 28% of organic sulfur from Baragolai coal. The coal samples were oxidized by H₂O₂ and HCOOH solution oxidation treatment. In this investigation, the oxidized coal samples were then pushed to a further desulfurization by solvent extraction (dimethyl formamide) and alkali (NaOH) treatment, respectively. After dimethyl formamide extraction, about 95% of inorganic sulfur and 31% of organic sulfur were removed from oxidized

Baragolai coal samples. However, nearly complete inorganic sulfur and 33% of organic sulfur was removed after NaOH treatment. The sulfur removal mechanism was that sulfur was oxidized to sulfones and sulfoxides during H_2O_2 and HCOOH solution oxidation treatment and then further removed by solvent extraction and alkali treatments.

Yazu and Takanohashi (Yazu *et al.*, 2015) found that the sulfur content in coal tar pitch was reduced by more than 15% by the oxidative desulfurization process using a urea-hydrogen peroxide complex with a carboxylic anhydride in Tetrahydrofuran medium. Pecina *et al.* (Pecina *et al.*, 2014) indicated that the removal of pyrite from a Mexican bituminous coal was successful in an oxidizing aqueous medium (sulfuric acid and hydrogen peroxide) combined with complex agents, such as quercetin, oxalic, and phosphoric and citric acids. The oxidation of pyrite plays a very important role in the desulfurization of Mexican bituminous coal in this situation.

Saikia *et al.* (Saikia *et al.*, 2013) used the per-acid ($\text{H}_2\text{O}_2/\text{HCOOH}$) medium to remove 38.09 % of total sulfur from high sulfur coals of North Eastern region (India). After $\text{H}_2\text{O}_2/\text{HCOOH}$ treatments, the treated coal was extracted with dimethyl formamide and alkali. As a result, alkali treatment could further decrease the content of total sulfur. In another study, Fallavena *et al.* (Fallavena *et al.*, 2012) also found that 88-98% of pyritic sulfur could be removed by using 10% $\text{H}_2\text{O}_2/0.1$ mol/L HCl which was a sour environment.

Carrillo-Pedroza *et al.* (Carrillo-Pedroza *et al.*, 2009) found that hydrogen peroxide and ozone could be also used as oxidizing agents to enhance the

desulfurization of Mexican sub-bituminous coal in acid solutions (nitric, sulfuric, and hydrochloric).

2.4. Electrochemical reduction

As shown in **Figure 3**, an innovative desulfurization process of coal water slurry using sodium metaborate electroreduction in the isolated slot was created by Tonghua Sun and his research group (Shen *et al.*, 2011 Shen *et al.*, 2012 Shu *et al.*, 2013). The sulfur in coal can be converted to H_2S and S^{2-} . The addition of divalent metal catalysts (Ni^{2+} , Mn^{2+} , etc.) could enhance the removal of S from coal water slurry. Sodium borohydride reduction desulfurization process for coal water slurry was also presented by Shen *et al.* (Shen *et al.*, 2011). About 47.8% of sulfate sulfur, 55.4% of pyritic sulfur, and 23.9% of organic sulfur could be removed through the optimum parameters using $NaBH_4$ reduction.

Li *et al.* (Li *et al.*, 2010) used sodium borohydride reduction to treat Yanzhou and Yanshan coal for the desulfurization process. The results show that the reduction of sulfate sulfur is the highest, and the reduction of pyritic sulfur is the middle, while the reduction of organic sulfur is the lowest.

Another innovative desulfurization process, called electron-transfer-induced desulfurization was used in the desulfurization of organic sulfur from sub-bituminous coal (Borah, 2006 Borah, 2004). The desulfurization reaction involved direct electron transfer from potassium ferrocyanide, $K_4[Fe(CN)_6]$. Increasing the temperature could enhance the sulfur removal. Some oxidized sulfur compounds, such as sulfoxide, sulfone, and sulfonic acid were formed in the aerial oxidized coals. As a result, the

desulfurization efficiency of oxidized coals showed a higher level of sulfur removal than that of unoxidized coal.

Khan et al. (Khan *et al.*, 2014) used cupric chloride for the desulfurization of lignitic coal from Habibullah Coal Mines, Lakhra, Pakistan. Maximum removals of total sulfur and organic sulfur were 50% and 56% at 150 °C. Maximum removal of pyritic sulfur was 66% at 200 °C. Both organic and pyritic sulfur were removed effectively by using cupric chloride. As shown in Eq. (1) (Lompa-Krzymien, 1982), the cupric ions can oxidize pyritic sulfur to sulfuric acid, which is washable:



2.5. Solvent extraction

Jorjani et al. (Jorjani *et al.*, 2008) used sodium butoxide to achieve the removal of organic and inorganic sulfur from Tabas coal. Artificial neural networks was used a research method to investigate the effects of operational parameters (coal particle size, leaching temperature and time, sodium butoxide concentration and pre oxidation time by peroxyacetic acid) on sulfur removal. At the optimum operational parameters, the removals of organic and inorganic sulfur were 49% and 84%, respectively. Jorjani et al. (Jorjani *et al.*, 2004) also found that combining air oxidation and peroxyacetic acid oxidation was the most effective method for enhancing sulfur removal.

Ehsani (Ehsani, 2006) investigated the effects of different reagents, $\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 , NaOH , CH_3OH , HNO_3 , and H_2O_2 , on the sulfur and ash removal from Tabas coals under reasonable pressure and temperature. It was found that $\text{Fe}_2(\text{SO}_4)_3$ is suitable for the desulfurization of fine distributed pyritic sulfur from Tabas coal.

Tripathi et al. (Tripathi *et al.*, 2002) studied the desulfurisation behavior of high-sulfur Indian coals by γ -radiation chlorinolysis in different media of chlorination (CCl_4 , $\text{CCl}_4/\text{H}_2\text{O}$, and $\text{CCl}_4/\text{CH}_3\text{OH}$) via radiolysis of CCl_4 . $\text{CCl}_4/\text{CH}_3\text{OH}$ was the most effective medium for the sulfur removal since CH_3OH could wet coal surface easier and show better penetration of chlorine into the coal structure which attacked more sulfur-containing sites. As a result, the maximum removal of total sulfur was achieved through $\text{CCl}_4/\text{CH}_3\text{OH}$ medium.

In another study, Das and Sharma (Das *et al.*, 2001) used sequential solvent extraction (morpholine - anthracene oil - N-methyl-2-pyrrolidone) to remove about 89% of organic sulfur from Assam coal. Most of the desulfurization was obtained by breaking physical sulfur bonds and not chemical sulfur bonds.

2.6. Low temperature pyrolysis

Liu et al. (Liu *et al.*, 2005) showed that the high-sulfur coal could be pyrolysis with potassium hydroxide or sodium hydroxide could achieve its desulfurization. After the pyrolysis process, the chars were washed with hot water for the further desulfurization process. Without the addition of potassium hydroxide or sodium hydroxide during the pyrolysis process, the sulfur removal was about 40-50%. However, the sulfur removal was about 70-80% with the addition of potassium hydroxide or sodium hydroxide in the pyrolysis process.

Sutcu (Sutcu, 2004) found that lignite with high organic sulfur content could be desulfurized by pyrolysis as the temperature ranged from 650 to 950 °C. The addition of limestone and dolomite in the pyrolysis process could remove more sulfur than the

addition of line. Meanwhile, the removal of sulfur in the atmosphere of CO₂ was more than that in the atmosphere of N₂.

2.7. Air oxidation

Pysh'yev et al. (Pysh'Yev *et al.*, 2007 Pysh'Yev *et al.*, 2004) investigated the significant effect of water vapor on the desulfurization process of sulfur-rich coal in the temperature range of 350-450 °C. A comparison of thermal oxidative desulfurization of coal was made between dry (4 vol % of H₂O vapor) and wet (30-70 vol % of H₂O vapor) atmospheres. It was found that some new iron-containing products (FeSO₄, Fe₂O₃, and Fe_{1-x}S) were formed in dry and wet atmospheres and water vapor could promote the transformation of pyrite to the iron-containing products. Some Fe₂O₃ and SO₂ were the products from the oxidation of FeS₂ at 673 K and higher temperatures. In another study, the chemical desulfurization of low sulfur coals using H₂O₂ solution was combined with the thermal desulfurization using mild pyrolysis and air oxidation pretreatments to achieve an effective sulfur removal (Nam *et al.*, 2004b Nam *et al.*, 2004c).

Thermal desulfurization processes of raw coal and Hg-treated coals (using HgCl₂ solution) were investigated by Borah et al. (Borah and Baruah, 2001 Borah *et al.*, 2001). Hg-treated coals showed more effective sulfur removal than raw coal and the C-S bond in organic sulfur was weakened during the thermal desulfurization processes with the temperature ranging from 50 to 150 °C in air. It was also found that mercury acted as a catalyst, which enhanced the formation of oxidized organic sulfur functionalities (S=O and -SO₂), as shown in **Figure 4**.

Zhang et al. (Zhang *et al.*, 2014) found the H₂S was formed under hydrolysis process since hydrogen could act as a catalyst in the formation of H₂S and more than 65% of sulfur in coal could be removed. Pal et al. (Pal *et al.*, 2003) also investigated the effect of coke oven gas, water gas, steam and pure hydrogen on the desulfurization of northeastern India high-organic-sulfur coal at temperatures ranging from 400 to 950 °C. Steam and pure hydrogen performed more effective sulfur removal than coke oven gas and water gas.

Wang et al. (Wang *et al.*, 1999) also found that the total sulfur removal from Lichuan coal was affected by the oxygen content in the mixture gas (mixture of oxygen and nitrogen) in semi-continuous reactor with the temperature ranging 623 to 823K. When potassium hydroxide was added as a promoter in semi-continuous reactor, the sulfur removal was not determined by the ratio of oxygen to nitrogen.

2.8. Microwave assisted

Wu et al. (Wu *et al.*, 2013) used microwave irradiation to treat high-sulfur coal for the sulfur removal and 25.91% of sulfur could be removed without the changes in the physical properties of coal. XRD results of coal samples before and after microwave irradiation showed that chlorite and FeS₂ could be converted to emery and magnetite. Chelgani and Jorjani (Chelgani *et al.*, 2011) combined peroxyacetic acid desulfurization with microwave irradiation pretreatment and obtained a more effective desulfurization of coal. The desulfurization time and temperature by peroxyacetic acid were the main factors on the reduction of sulfur. During the processes of microwave irradiation pretreatment and peroxyacetic acid desulfurization, coal organic matrix

was not changed whereas both inorganic and organic sulfur were significantly removed.

Mi and Wei (Mi *et al.*, 2011) indicated that microwave irradiation had significant effect on the removal of both inorganic and organic sulfur from coal. It is well known that the microwave irradiation time and irradiation power are the most important factors determining the desulfurization efficiency (Mi *et al.*, 2011 Jorjani *et al.*, 2004). Therefore, microwave irradiation time and irradiation power should be controlled in the microwave assisted desulfurization (Zhang *et al.*, 2014).

2.9. Ultrasonic assisted

Mi and Kang (Mi *et al.*, 2012) used ultrasonic irradiation to pre-treat lu'an coal and then the treated coal was sent to microwave irradiation assisted desulfurization. The results showed that pretreatment of coal by ultrasonic irradiation could enhance the sulfur removal during microwave irradiation. It is recommended that ultrasonic irradiation can be added as a pretreatment method in microwave irradiation assisted desulfurization. Mi *et al.* (Mi *et al.*, 2007) also used ultrasonic and microwave pretreatments to promote the extractive desulfurization of four Chinese high sulfur coals. The combination of ultrasonic and microwave had a positive effect on the extractive desulfurization. The increase of ultrasonic treatment time and power could increase the desulfurization rate which was reduced by the increase of coal particle size.

3. Summary

Chemical-related desulfurization methods include acid and alkaline leaching,

H₂O₂ oxidation, electrochemical reduction, solvent extraction, pyrolysis, air oxidation, microwave/ultrasonic assisted. They are effective for both inorganic and organic sulfur. However, they are only used in laboratory not in industry now. Forwarding chemical desulfurization methods into industrial desulfurization needs long way and time to achieve. The chemical desulfurization of coal can be also assisted by microwave and ultrasonic pre-treatment in order to enhance the desulfurization rate. Low temperature pyrolysis and air oxidation can remove some of organic sulfur. They have a potential application in the future as low rank coal is usually heated for the dewatering before its use. Low temperature pyrolysis and air oxidation can be combined with the dewatering processes to upgrade the quality of coal, including the dewatering and desulfurization. Various desulfurization methods can be combined for achieve an effective sulfur removal.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51604272), the Fundamental Research Funds for the Central Universities (YC150002), and A Priority Academic Program Development of Jiangsu Higher Education Institutions.

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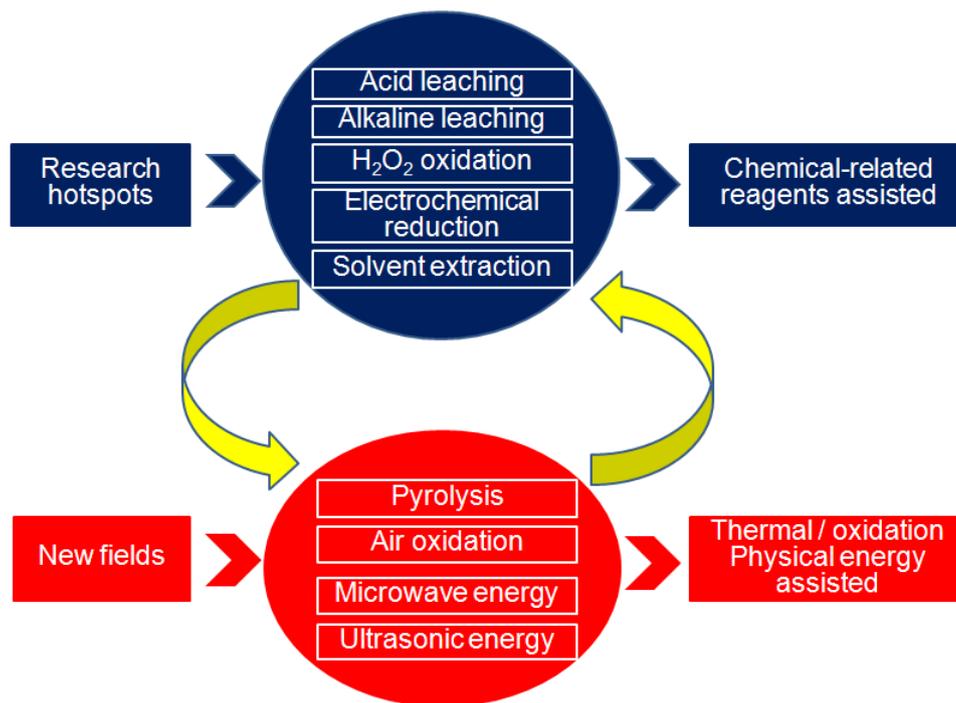


Figure 1 Classification of coal chemical-related desulfurization technologies

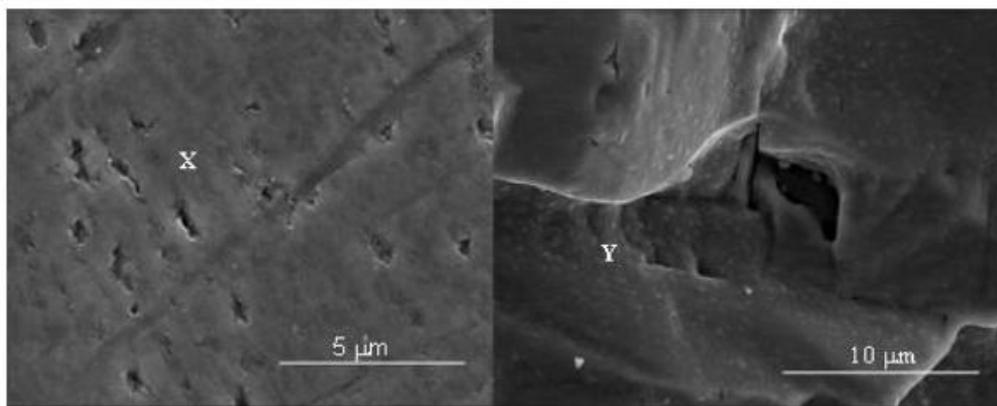


Figure 2 SEM microphotography of untreated and preoxidized pyrite. (Left) Untreated pyrite; (right) preoxidized pyrite (Conditioning time of 20 minutes in 0.5M H_2SO_4 and 1M de H_2O_2) (Davalos *et al.*, 2009)

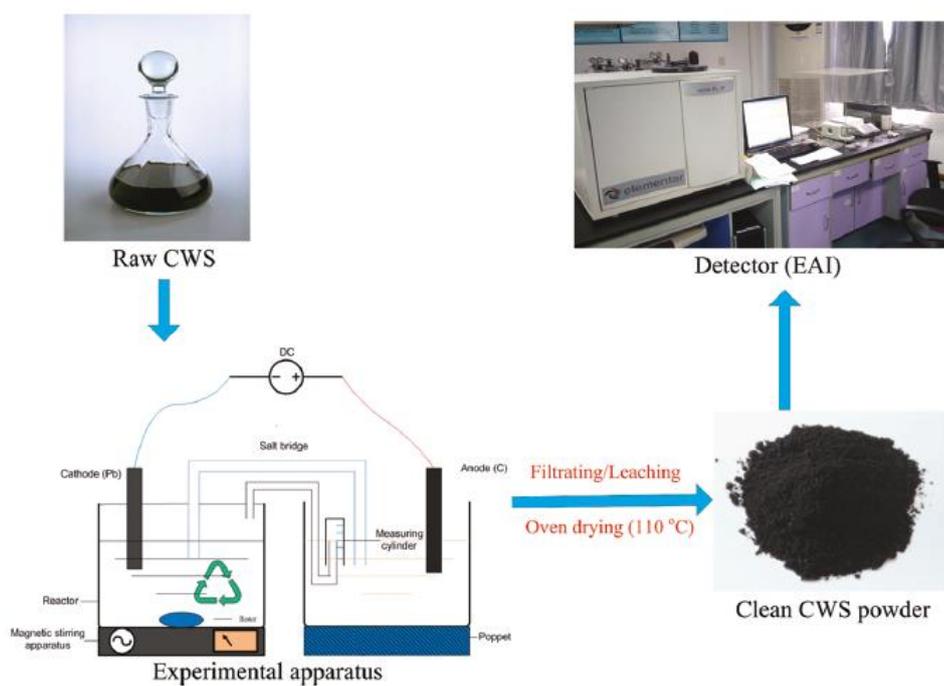
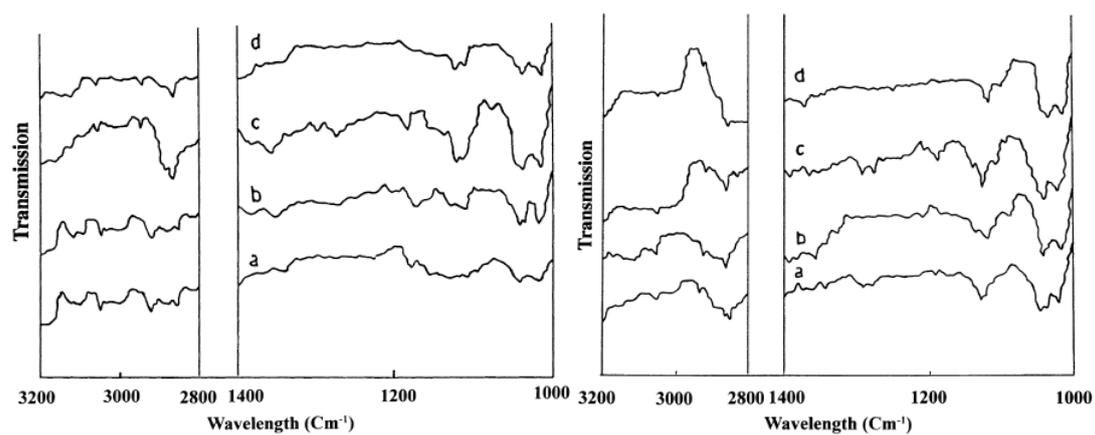


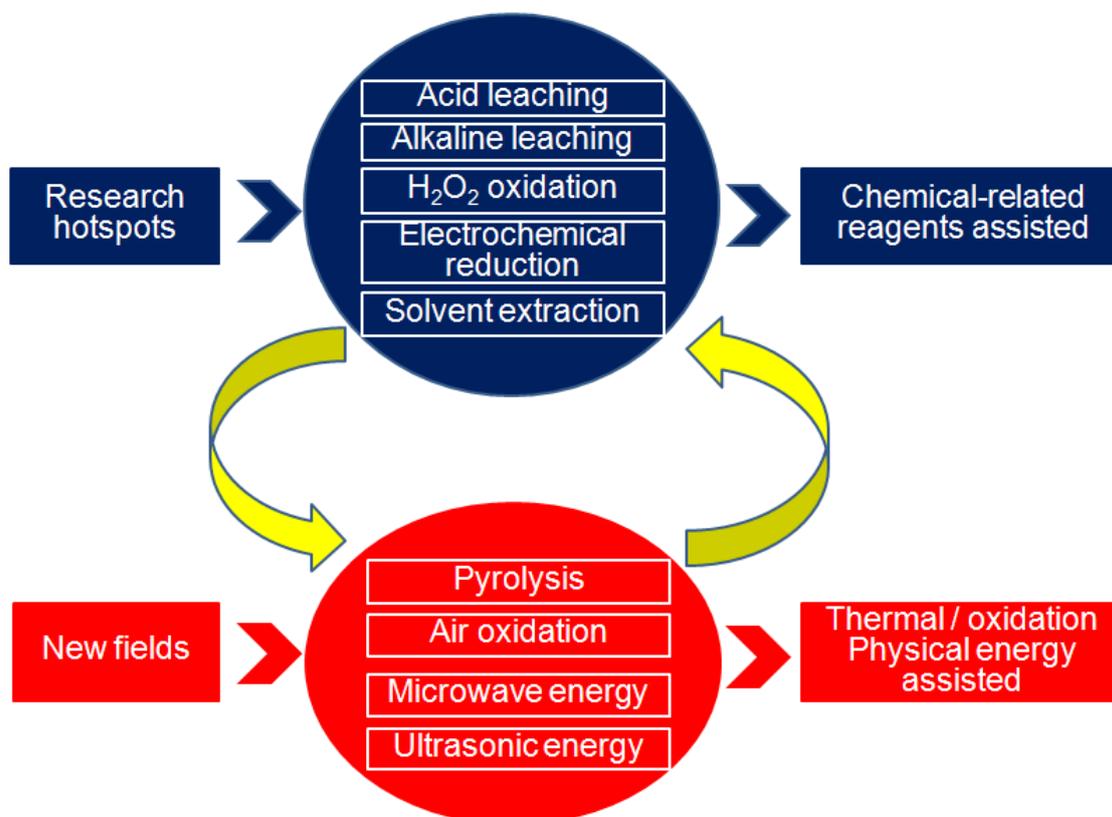
Figure 3 Schematic of the electrochemical reductive desulfurization apparatus and general procedure (Shen *et al.*, 2011)



(I) feed coal samples

(II) mercury-treated coal samples

Figure 4 Infrared spectra of feed and mercury-treated coal samples: (a) unoxidised (25 °C); oxidised at (b) 50 °C; (c) 100 °C; and (d) 150 °C. (Borah *et al.*, 2001)



Graphical Abstract

Highlights

- This review highlights advances in chemical-related desulfurization of coal.
- Chemical-related desulfurization is effective for inorganic/organic sulfur removal.
- Various desulfurization methods should be combined for effective sulfur removal.