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Chapter 9

Reverse Flotation

Fatma Deniz Öztürk

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Abstract

Reverse flotation of coal can be explained as a process where valuable minerals are depressed, while undesired and unhealthy minerals are floated with the help of some reagents. Nowadays, conventional enrichment method of coal could not achieve removing unhealthy minerals partially from internal structure of coal such as sulfur, Hg, Au, which propagate in air after burning treatment, or heavy metals such as Be, Cr, Ni, As, Cd, Co, Ni, Sb, Se, Pb, Co, Cl, Be, Ba, which involve in water and soil where habitat and human health can directly be influenced from them. In fact, reverse flotation of coal enables to remove these undesired mineral content from coal structure not only in macro size but also in micro size. On the other hand, like undesired minerals, valuable ones like vanadium, germanium, etc. are also taken from coal particles by using the same procedure. Thus, with all these respect, reverse flotation is considered as an alternative and innovative solution for coal beneficiation especially for low rank coal since low rank coal is more compatible for reverse flotation because of being more hydrophilic which means tendency to float is less. Around the world wide, most of the coal reserves belong to low rank coal, so application of reverse flotation is becoming more inevitably common in future.

Keywords: coal, reverse flotation, mineral matter, collector, depressant, frother

1. Introduction

Coal is a type of sedimentary rock, which exists in nature in the form of black-dark gray and brown-black color and consumed as fossil fuel. Besides, coal possesses carbonated plants, and its proportions in terms of weight and volume are more than 50 and 70%, respectively [1].

Raw coal is enriched by different beneficiation methods that are mainly gravity-based separation and flotation. In gravity-based separation, undesired substances, which are not compound of coal, might be reduced but it could not be effective on ingredients being in internal

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structure of coal. It is dangerous to consume raw coal as fossil fuel for environment due to high amount of sulfur ingredients, because impurities like sulfur produces harmful gases after heating process. Therefore, in order to remove these undesired contents, flotation is applied as an enrichment method.

Flotation, as the name implies, is expressed like separation of substance in compound form by floating process. Floatability of material is crucial aspect for efficiency of flotation. For coal mineral, some of them have natural floatable properties because of its nature, but some others do not possess an inherent floatability because of its internal structure properties [2–4]. The surface texture of coal particle may involve both hydrophobic and hydrophilic zones. Thus, domination of this zones is one of the criteria which decides whether coal is floatable or not [5, 6].

Another criterion for defining floatability of coal particle is moisture content. For example, lignite, which involves 70–80% carbon, has high moisture content and extremely less hydrophobic disposition. The chemical structure of lignite is altering due to elimination of polar groups like hydroxyl and carboxyl groups, and natural moisture content decreases during the transition from lignite to bituminous coal. As a result, coal comes in position of more hydrophobic. Moreover, the content of carbon is in relation with hydrophobicity of coal, too. In the range of 81–89% of carbon content, polar character loses its influence, and coal becomes more hydrophobic. Hydrophobicity of coal reaches its maximum level in 89% of carbon content, and it decreases slightly when the carbon content climbs up from this level. The flotation is directly related with the floatability of particles, so higher carbon content makes conventional flotation process easier [7, 8].

In addition, flotation efficiency is directly related with the properties of the inorganic and organic mineral impurities existed in coals and amount and dispersion of gangue mineral inclusion. It is not possible to remove these finely dispersed impurities inclusion by applying physical methods [9], so flotation should be taken in consideration inevitably in the manner of protecting environment and recovering valuable minerals.

In this respect, flotation is playing significant role in supplying raw materials for various industries. More than 2 billion tons of minerals and fine coals are being processed annually by using flotation in worldwide [10]. For this reason, flotation becomes one of the most important methods for enrichment of minerals and is commonly used in the world [10–13]. At the same time, flotation is utilized for finely-grain-sized coal upgrading [14–18], fly ash decarburization [19], and wastewater treatment [20]. Since coals and ore are liberated in fine grain size, tendency to flotation in mineral processing increases [21].

For environment, sulfur and ash content of coal is too important because heating process leads to propagate harmful gases to the environment. Flotation is one of the effective methods for desulfurization and deashing of raw coal having high ash and sulfur content [22]. Flotation properties depend on the surface texture and other features of particle, so to make particle float or depress in pulp, some different reagents are governed. In conventional flotation, oily collector and frother are used, and these reagents are conditioned in a period of time [23, 24]. In flotation of low rank coal, it is difficult to obtain good result using oily collector

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due to surface of minerals with low surface hydrophobicity [23]. For this reason, collector consumption is much more in flotation of low rank coal compared with high rank ones [25]. In low rank coal flotation, in order to increase performance, parameters like grain size, pulp density, reagents type and dosage, pulp pH, flotation and time conditioning, and air entrainment rate should be investigated, and [9, 22, 26, 27] most proper condition should be determined with respect to results of them. In addition to conventional flotation method, reverse flotation is also applied on enrichment of minerals.

The reverse flotation was commenced to investigate in 1950s [28, 29]. In following studies after 1950s, different researchers also continued to work on that concept [30–34] and still have been proceeding [4, 25, 27, 35–43]. However, researchers have not understood completely how particles inside the pulp interact with each other, yet because there are many uncertain factors that influence the surface of minerals and coal existing in pulp. Foremost among these factors is that coal possesses different type of elements and behavior of these elements has not been identified; thus, theoretical and experimental verification of interaction between elements is difficult. For that reason, more researches should be performed in that regard. Studies until current time are generally associated with reduction of pyrite and ash. However, recovery of valuable elements in coal should also be taken into consideration in the environmental aspect as well, so the objective of this study is to discuss the benefits of reverse flotation of coal for environment on the behalf of past researches.

2. Process of reverse flotation

2.1. Ash reduction

Ash content is important for both environment and flotation efficiency. Ash content in coal can be eliminated by both physical methods and flotation process, but the presence of ash in internal structure of coal particle could not be removed by physical methods. To be able to remove impurities inside coal particle, reverse flotation is applied on coal. In reverse flotation, tailing is taken as clean coal, and concentrate is accepted as gangue minerals.

Ash content is crucial for coal flotation efficiency. Froth is the key element of determining flotation concentrate, and between concentrate froth and the ash content, there is a strong relation [44].

Ash reduction in reverse flotation of coal subjects have been developed for 30 years by some important researchers. Stonestreet, Pawlik, and Ding have performed intensive studies on ash reduction in reverse coal flotation. Stonestreet and Pawlik prepared their PhD thesis on reverse flotation of coal separately [4, 45] and continued his studies with Franzidis in advance [39–41]. In their experiment, clean coal with 7% ash and silica were mixed as a feed, and quantity of each element was same. From the results of experiments, reverse flotation process, 92% ash reduction was achieved from feed in which ash content was 54%. In depressed coal, ash content was 12%, whereas the recovery of coal is 27%. Results of experiment show that recovery of coal was not good even it was achieved that high ash reduction was obtained

[39]. They continued their experiments to increase the recovery of coal by using three stage addition process, and for same substance, a product of 86% coal throughput involving 12% ash was obtained [40]. Within the matter of improving reverse flotation, they extended their studies and compared the laboratory column cell using synthetic feed mixture consisting coal and quartz. Thus, recovery capacity of coal was much better than in normal flotation [41].

Later, Ding and Laskowski took Stonestreet's studies step further by adding dolomite and calcite as gangue minerals and surveyed the effects of factors on separation. They used dodecyl trimethyl ammonium chloride (DTAC) as a collector whose properties of separation are good when it is used minimum 6 kg/t [2]. After, Ding further continued to study on reverse flotation using DTAC on subbituminous coal, too. DTAC consumption was dramatically descended from 6 to 1.375 kg/t by applying polyacrylamide (PAM) and zero-conditioning time method. Besides, in order to improve selectivity, dextrin was governed, and the addition of tannic acids as a dispersant improved the quality of concentrate. For the feed ash content of 34.6%, the concentrate of 16.7% ash at 50.4% yield was acquired [36].

On the other hand, Patil and Laskowski carried out their studies regarding to enhancing reverse flotation of coal. Patil drew on dodecyl trimethyl ammonium chloride (DTAB) in reverse flotation as collector, but used no depressant, first. Also, zero-conditioning time method was applied in their studies. Zero conditioning was accomplished by adding necessary quantity of DTAB in one step, immediately after system was exposed to the air. The logic behind the zero-conditioning time is that continuity of reverse flotation should not be interrupted in any case. Air bubbles formed from air introducing carried collectors, DTAB, during the flotation process. The entrainment of DTAB carried in air bubble demonstrated that reduction of ash from sub-bituminous coal (LS-26) from 34.7 to 22.9% with gangue yield of 36.8% by using any depressant. In the existence of depressant which was dextrin with 0.5 kg/t, the ash substance of LS-26 was reduced from 34.7 to 16.5% at the clean coal yield 55% [46].

Generally, researchers have been seeking the behavior of ash particles under the participation of different reagents. They mainly focused on low rank coal like lignite due to their hydrophilic properties. Vamvuka also studied on lignite and oxidized coals and used dodecyl amine (DDA) with kerosene in flotation. Ash reduction of 18% with coal recovery of 80% was achieved [47]. Ozturk also proceeded their studies on reverse flotation of Turkish lignite samples involving high ash and sulfur content. They used ionic collector (Aero 3477) and obtained clean coal product of 29.04% ash at a combustible yield of 78.14%, while with non-ionic collector [kerosene], these values altered to 27.04 and 81.19%, respectively [27]. On the other hand, Zhang et al. also worked on reverse flotation, but used different reagents, as a collector dodecyl amine chloride (DAH), as a depressant corn starch, and as a further methyl isobutyl carbinol (MIBC), and observed the effect of particle size in the presence of soluble salt. When the highest reverse flotation performance was achieved, concentrate ash content of 11.30% was obtained with a combustible recovery of 65.29% [43]. Finally, Xia et al. applied reverse flotation on taixi oxidized coals. Dextrin was used as depressant, whereas hexadecyl trimethyl ammonium bromide (HTAB) was oriented as collector [42].

Alternatively, Li studied with sub-bituminous coal involving a significant amount of oxygen which causes to decreasing hydrophobicity. Due to being difficult to upgrade fine fraction

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in normal flotation, reverse flotation method in which minerals was made hydrophobic by adding collector, whereas coal was made hydrophilic by adding depressants. Li commenced experiments preparing mixture from coarse coal with fine quartz and medium size coal with fine silica. Ash content was dropped around 35% while recovering nearly 85% of combustible material by reverse flotation. The obtained results were much better than that acquired from conventional flotation method. However, when same procedure was applied to fine coal and quartz, separation was not as effective as tests prepared with coarse coal due to influence of hydraulic entrainment [48].

2.2. Sulfur removal

In the early age of 1960s, Eveson was the first person who took attention on reverse flotation by removing shale from bituminous coal. After, reverse flotation had become popular among other researchers, and they started to focus on desulfurization of coal by using this method [30–32, 49].

The presence of sulfur in coal might be found in three forms which can be categorized as organic sulfur, metallic sulfur, and sulfatic sulfur [9, 50–53]. Organic sulfur in coal originates from carbonated plant, while metallic and sulfatic ones' source is inorganic sulfur which exists among mineral compounds. The most common example of metallic sulfur is pyrite and it is called as pyritic sulfur. In addition to pyrite, other minerals may be involved in coal structure such as marcasite, galena, sphalerite, etc. For sulfatic ones, gypsum may be illustrated [54].

The sulfur content is varying by different types of coal, and sulfur content accounts for pyritic and organic sulfur amount in coals. Even coal substances might be extracted from same ore bed, they possess different sulfur content. Pyritic sulfur may represent 20–80% of total sulfur content [38, 50]. Like ash, pyrite particles may also exist in internal structure of coal, so physical methods are becoming nonfunctional in removal of pyrite from coal substance [28]. Flotation was started to be applied to achieve desulfurization as well.

Each type of pyrite mineral shows different floatability properties, and the reason of that was investigated by some important researchers. Feurstenau considered that the cause of that variation is related with the formation of elemental sulfur. Because of being naturally hydrophobic [37, 55, 56], elemental sulfur can conduct with the surface of pyrite, and then, it may behave like a collector for pyrite. Oxidation of pyrite under proper condition forms elemental sulfur, and it is frequently observed in weathered coal, not in fresh coal [57]. Two basic reactions are standing below for expressing elemental sulfur formation from pyrite. These are as follows:

$$2\,Fe^{+3}(aq) + FeS_2 \;=\; 3\,Fe^{+3}(aq) + 2\,S_{(s).} \tag{1}$$

Eq. (1) accounts for formation of elemental sulfur under microbial oxidation of pyrite, i.e. pyrite oxides in moist. To proceed the process of oxidation, acidic environment is necessary because pyrite-oxidizing bacteria can grow under this circumstance [37, 38]; that means, during the pyrite oxidation, iron sulfates, type of salts, constitutes, and these are known as flotation

depressant [55]. These depressants can only be dissolved when acidic conditions are satisfied in pulp. On the other hand, unlike formation of sulfate format, if elemental sulfur formation is obtained at the end of oxidation, it is assumed that reaction of coal pyrite is similar to reaction of mineral pyrites, and flotation can be carried out on neutral pH range [37]. Second oxidation reaction may take place with water [58], and it is expressed in the form of;

$$FeS_2 + 3\,H_2O = Fe(OH)_3 + 2\,S^o + 3\,H^+ + 3\,e^- \quad (2)$$

In both cases, if conditions are suitable, substantial quantity of elemental sulfur formation on pyrite sulfur can be observed even the elemental sulfur is normally an intermediate product in a series of reactions that are over with producing sulfate (SO_4^{-2}) [37].

Pyrite has small hydrophobic tendency [55, 59–61] when its surface is unoxidized. With the presence of water, oxidation takes place on surface of pyrite and forms ferric hydroxide, which leads to decreasing hydrophobicity [62–64]. In pH range of 4.5–6.9, oxidation products of pyrite act like strong depressant [60], as it was mentioned before. In order to enhance hydrophobic tendency of pyrite, it is required to add some collector like xanthate [65] since floatability of pyrite intimately depends on pH, and highest floatability might be obtained in acidic pulp [38].

Kawatra performed experiments on fresh coal and 1-year aged coal for different conditions. Fresh coal substances were exposed to different pH levels, and the percentage of froth weight being in directly proportional with floatability of pyrite were investigated. pH levels were defined as 8.3, 7.5, 2.3,2.2, and 2.0, and froth weights were found as 5, 4, 98, 98, and 99%, respectively. On the other hand, same procedure was applied on 1-year aged coal at -15°C, and lowest weight was attained around 37% when pH was almost equal to 6.8, whereas pH was dropped to 2.0, achieved weight dramatically increased, and equal to 92%. Lastly, 1-year aged coal substances were heated up to 100°C and tested in pH level 6.2 and 2.0, and results were 7% and 82%, respectively. From the results, it can be understood that freshly ground mineral pyrite is not readily floatable at neutral pH despite of being highly floatable in acidic pH. On the other hand, pyrite oxidation concludes with sulfate formation, which is not hydrophobic. If necessary conditions might be satisfied for forming elemental sulfur, pyrite can be floated. Also, it is shown that under certain condition, pyrite can be floated at neutral pH, but that is not a normal case. [37]

2.3. Vanadium recovery

Vanadium is strategic metal and has been extensively used in the field of steel and alloy industry. Tensile strength capacity of vanadium is too high, so 80% of vanadium are utilized for alloy steels, whereas remaining portion is applied in chemical industry [66–68].

Vanadium is another element that might be recovered from coal by using reverse flotation. Coal vanadium element can be found in some coal minerals such as illite, muscovite, roscoelite, and kaolin in the form of isomorphism, whereas tantalite and garnet are appeared in the form of absorption [69]. In addition, quartz, calcite, and carbonaceous are found to be main gangues in stone coal [68]. For many studies, flotation has been popular topic for many years, but there are not much more available studies on pre-concentration of vanadium in low-grade coal by the method [70].

Stone coal was exposed to the two stages of flotation processes to recover vanadium microelement. Mineral composition of coal was calcite, barite, quartz, and V-minerals. Reagents were sulfuric acid (pH regulator), oleic acid (Ca minerals collector), sodium silicate (dispersant), sodium fluorosilicate (SFF and depressant), melamine (EA and V minerals collector), dodecyl amine (DDA and V minerals collector), octadecylamine (DC and V minerals collector, terpenic oil (frother)). pH was kept between 7 and 8, and water glass was used as depressant (2000 g/t). Besides, oleic acid was taken 200 g/t as collector [70].

At the end of this study, selective separation of vanadium-bearing minerals can be achieved in pH 3 using melamine (EA). The final vanadium concentrates with V_2O_5 grade of 1.88% and recovery rate of 76.58% are obtained by desliming-flotation process and 72.51% of the raw ore is rejected as tailings [70]. Also, results of other tests demonstrate that grade and recovery of V_2O_5 concentrate are 1.32% and 88.38, respectively, and tailing yield is 38.36%. On the other hand, recovery and grade of carbon mineral which may be used as fossil fuels are 75.10 and 30.08%, respectively [71].

Although vanadium recovery from stone coal is exploring recently by researchers, studies have already been demonstrated how well vanadium is recovered and obtained clean coal simultaneously.

2.4. Effects of rank, mineral, and maceral

Coal quality is determined by many properties, but major factor is coal rank. The rank of coal is identified by the percentage of fixed carbon, moisture (water), volatile matter, and calorific value in British thermal units after sulfur and mineral matter content have been subtracted. Coal types that might be ordered from lowest to the highest rank are lignite, sub-bituminous coal, bituminous coal, and anthracite [72]. Rank directly influences floatability of the coal since chemical structure changes due to elimination of polar groups during coalification process. At the end of this process, carbon content increases, and result in increasing hydrophobicity [73, 74]. Although, rank and floatability are directly proportional, highest hydrophobicity is achieved in bituminous coal, not anthracite, which has highest coal rank, but difference in floatability is not significant between them [75, 76]. Bituminous coals are enough hydrophobic to be floated in further without collector, but in order to improve coal recovery, collector oil is governed [77] even it reduces the coal rank [78].

Moreover, degree of the oxidation of the coal surface is essential for hydrophobicity. It leads coal to act like lower rank coal whose hydrophobicity is lower [4, 79, 80]. However, there are some cases that oxidation increases in the floatability of coal like freshly cleaved coal surfaces. Short-time air exposure may increase hydrophobicity due to drying of the coal surfaces which then becomes more difficult to wet [9].

Coal is composed of many different minerals that influence type of beneficiation method and its applications. These materials cannot be removed from coal totally by using conventional method [81]. Coal has heterogeneous structure, but is mainly formed from inorganic materials such as clay, quartz, sulfides, and sulfates [82, 83]. Mineral content determines the coal grade, and its rate should be less than 50% to be accepted as coal [54]. There are more than

120 minerals involved in coal, and primary ones regarding their degree of presence are quartz, kaolinite, illite, montmorillonite, chlorite (may contain Mn), clays (may also contain Be, Ni, and other trace elements), pyrite (may contain As, Cd, Co, Hg, Ni, Sb, and Se), calcite, and siderite (may contain Mn); not common ones are analcime, apatite, barite, chalcopyrite, clausthalite, crandallite, floricide, gorseksit, goyasite, dolomite, feldspar, galena, marcasite (may contain same elements as pyrite), monazite, rutile, sphalerite (may contain Cd), xenotime, and zircon; and rare ones are chromite, gypsum, gold, gibbsite, rock salt, magnetite, and muscovite [72]. Seventy-six elements of periodic table can be found in coal substance. Some of these are trace elements and their ratios are expressed with ppm. Some trace elements may be concentrated in specific coal bed, which make that bed a valuable resource for those elements such as silver, zinc, or germanium [84]. However, some elements have potential to damage environment like cadmium or selenium if their concentrates are more than trace amounts. Trace elements associated with clays or pyrite are removed from coal by flotation process, and it is significant to dispose all trace element with in the manner of environment and recovery of valuable elements. Nevertheless, except for gypsum, the various forms of ash and germanium, recovered minerals have not been used commonly [72].

In addition to rank and mineral matter, maceral also affects the flotation of coal since coal hydrocarbon structure and hydrophobicity are influenced by maceral content [78, 85]. The macerals consist of lithotypes, and their proportions vary. The properties of lithotypes also differ from each other. Macerals are classified into groups according to dominant components, which are vitrine, inertinite, or liptinite, and has different hydrophobicity. For example, the lithotype fusain involving inertinite group macerals is generally the least floatable, whereas vitrian involving vitrinite group macerals is the most floatable [75]. Studies associated with maceral recovery proved that it is possible to regain good volume macerals without much loss of combustible value [83]. The studies on floatability of coal macerals were appeared at the beginning of 1950 by Horsley [8] and Sun [86]. According to Burdon, maceral content changed with increasing time flotation [87]. Even in same flotation cell, maceral content could vary when samples were taken from different place of it [3] because the macerals are the basic microscopic, physically distinct, and chemically different constituents of the carbonaceous matter in coal, which originate from material deposited in the primeval swamps [83]. Due to variance in maceral content, it is essential to define coal nature and response each maceral during the flotation. Based on maceral content in clean coal, the use of coal can be optimized. For example, high liptinite content increases the calorific value, whereas high inertinite content in concentrate stimulates increase in fixed carbon [88].

Rank, mineral content and macerals are influencing the flotation performance and type because these are essential parameters for floatability of coal. Reverse flotation can be optimized for low rank coal because low rank coal can be suppressed more easily since hydrophobicity of low rank coals are more less due to its polar structures. In order to recover valuable minerals and remove hazardous minerals at the same time, reverse flotation is again proper way because mineral content of low rank coal is more compared to high rank coal, so minerals might be floated without taking much more effort. Lastly, macerals can be divided into some groups according to compounds content as it was mentioned before. Coal with lowest floatable maceral, fusain, may be upgraded by using reverse flotation, too.

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2.5. Effects of pH

The pH has great importance in flotation because pH of liquid phase influences the surface characteristics and behavior of mineral and induces minerals to absorb all types of reagents on the surface. Response of reagents to the pH is essential for flotation, and there are no standard pH values for particular minerals in flotation. Instead, it is generally expressed with range for flotation of specific minerals, and it may differ according to participating reagents. For this reason, this may become complicated and needed to perform sensitive when highly selective products are required. Like coal reverse flotation, effects of hydroxide ions (OH−) and hydrogen ions (H+) ions are not only important for floating mineral matter but also important for suppressing coal [89]. Mineral surface can be altered with adjusting these ions in pulp. Minerals in pulp can be charged positively or negatively by arranging pH regarding the isoelectric point (IEP). When the pH is higher than IEP, minerals charge negatively, on the contrary, opposite actions will take place in mineral charging. Zeta potential is related with absolute changing in pH with respect to IEP, so it increases slowly [90, 91].

The pH plays important role in pyrite removal, which is hazardous mineral for environment. Mineral pyrite and coal pyrite act different. Inherently, mineral pyrite is floatable, and it loses its floatability when pH is greater than 5.0. When the pH range is between 5 and 9, the recovery of mineral pyrite is not noticeable even neutral oil collectors are utilized to render mineral pyrite floatable. Although same fashion is used for coal pyrite, it does not act as mineral pyrites. In the pH range of 2.2–8.8, coal pyrite can be recovered 31–43%, whereas mineral matter pyrite can be achieved to regain 99% over the same pH range. Kawatra carried out microscopic examination of coal pyrite flotation and resulted in floated materials that were coal and locked coal/pyrite particles. Therefore, it is assumed that coal pyrite was floated due to attachment to coal [38]. Chander and Aplan performed studies to prove that pyrite is inherently less floatable due to exposed oxidation during purifying from coal which may result in destroying floatability of pyrite [34]. The studies show that coal pyrite may be floated due to locked or entrained particles [38]. Some experiments were handled by Kawatra to examine the effects of pH with using different reagents. In the first experiment, the pulp pH was arranged lower than 4.0, and fuel oil was used as collector for mineral pyrite. Flotation could be achieved with the range of that pH, but native floatability was entirely lost with higher pH values. In second trial, coal pyrite was tried to be floated. However, coal pyrite may behave like mineral pyrite, and it was not recovered at neutral pH range [38].

The effects of surface and solution chemistry of Fe(II) and Fe (III) ions on the flotation of both mineral and coal pyrite with xanthate were investigated based on flotation output, zeta point measurements, and thermodynamic calculations. The results showed that existence of ferrous and ferric ions induced pyrite depress in pH range 6–9.5. Coal pyrite was recognized non-floatable above pH 6 due to large number of ferrous ions resulted from pyrite oxidation. Moreover, thermodynamic calculations demonstrated that formation of ferric hydroxyl xanthate leads to reducing floatability of pyrite when the pH is greater than 6.0 [92].

On the other hand, some additional experiments have been performed for different types of minerals existing in coal structure. As it is well known that materials vary between each other with respect to their properties. Like pyrite, ash also can be recovered by reverse flotation

along the different pH ranges. Stonestreet performed studies on ash reduction by applying reverse flotation method on quartz coal mixtures with same amount. The result of their studies showed that maximum ash reduction was succeeded using talk water whose pH was equal to 7.6 [4]. After, Pawlik also touched upon ash reduction with different coal substances. Sub-bituminous, bituminous, and oxidized bituminous coal were objective of reverse flotation with different pH ranges. At first, bituminous coal were exposed to different pH ranges, and optimal results for normal and oxidized coal differed. For normal bituminous coal, the flotation yield went into decline for higher pH values than 9.5. However, sharp decrease was observed when pH level becomes higher than 4.0 for oxidized bituminous coal sample. Besides, different tests were performed for sub-bituminous coal/silica mixtures, and for these tests, optimum pH range was determined between 8.3 and 8.6 [25]. Moreover, Ozturk mainly focused on ash reduction by reverse flotation of lignite, and they achieved maximum level of reduction at neutral pH range around 8 [27]. Same with Ozturk, Zhang also implemented reverse flotation on lignite sample at neutral pH level [73]. Lastly, sub-bituminous coal/quartz mixture with ratio 7:3 was subjected to the test, and all tests were done at neutral pH level [48]. Some additional examples are given from different pH ranges to represent bad results. For example, the low ash content of concentrate was obtained around 10.5 pH value due to optimum flotation of calcite and dolomite around this pH [93].

As well as ash and pyrite, some other valuable minerals can also be regained by reverse flotation throughout different pH levels. Ding worked on sub-bituminous coal sample with 48.5% ash content and gangue minerals such as calcite dolomite and silica with the ratio of 7:1:1:1, respectively. These gangue minerals were intended to be floated. In first study, when pH was 10.4, these gangue minerals can be floated [35], whereas in second test, zero-time conditioning was also taken into consideration, and maximum yield was achieved at the 7.5–8.4 pH range [36]. Wang also tried to float calcite as well as vanadium, which has great value in industry. For calcite, pH level varied between 7 and 8, while it was 3.0 for vanadium [70].

Therefore, importance of pH is clearly explained by studies, and more research should be carried out to take a step further in reverse flotation.

2.6. Effects of particle size

The most important criteria of mineral processing is associated to size of liberated mineral particle. The performance of flotation process depends on the degree of liberation of mineral in fine fraction. For this reason, flotation is applied to minerals that are intended to recover or remove from coal. Coal has a complex structure and possesses various minerals. Although the particle size of coal is generally less than 0.5 mm, liberation may not be achieved in that fraction size, so grinding may become inevitably for well separation. Hence, it is compulsory to apply flotation on coal due to liberation in fine fraction phase. However, finer fraction does not always mean that every parameter related with flotation is obtained in well range. There is a trade of between fraction size and performance of flotation. In **Table 1**, some studies with different coal type associated with various fraction size are demonstrated.

Zhang et al. studied on lignite which possessed 42.34% ash content by applying reverse flotation. Recovery amount and flotation performance can differ with respect to particle size.

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Coal type	Particle size (micron)	Floated minerals	Reference
Sub-bituminous coal/quartz	150–200 (coarse coal), 74–120 (medium size coal)	Mineral matter	[50]
	−38 (fine coal), −200 (raw coal)		
	−56 (fine silica), −200 (coarse silica)		
Lignite with 42.34% ash content	−425, 250–425, 150–250, 150–74, 74–45, −45	Ash	[43]
Lignite	100 (86% of material finer mineral than 100 micron)	Ash	[27]
Low grade stone coal (mass fraction)	−38, 38–50, 50–74, 74–154, 154–300, +300	Carbon, vanadium	[71]
Low grade stone coal	−38, 38–50, 50–74, 74–154, 154–600, 600–1500, +1500	Carbon, vanadium	[70]
Taixi oxidized coal	250–500, 250–125, 125–74, −74	Mineral matter	[42]
Lignite	+300, 300–75, −75	Ash	[47]

Table 1. Particle size of minerals participating into the reverse flotation.

Maximum performance was obtained for −74-micron fraction size with the combustible recovery of 65.29% and ash content of 11.30% after 20 minutes flotation. However, maximum flotation rate constant was achieved in 150–250-micron range, and the maximum reverse flotation index efficiency was attained for −425 microns. Hence, combustible recovery increased with increasing size fraction but meanwhile the concentrate ash content also increased particularly for finer particle sizes [73]. For finer fraction, slime problem appears. Because of that reason, there must be performed detailed studies for finer fraction flotation in order to obtain optimum results.

2.7. Reagents (collectors, depressants, and frothers)

The purpose of using reagents is to change the surface properties of minerals to adjust which material is floated and depressed. In this concept, regulator reagents (pH adjustor, activator, depressants, and dispersants) are entrained into flotation process to improve quality of selectivity and separation. In **Table 2**, reagents are demonstrated in three groups: depressants, collectors, and frothers. Most of reverse flotation experiments are listed, and for each test, available used reagents are indicated (**Table 3**).

Collectors are the reagents, which cause to arranging hydrophobicity of material. Collectors can be observed into two main topics that are ionic and non-ionic collectors. Non-ionic collectors are organic compounds formed from hydrocarbon chains having no neutral and polar groups, whereas ionic collectors are divided into two groups, anionic and cationic. The surface properties of minerals determine the reagents selections, and after necessary conditioning is done, flotation process starts. Some of the preferred collectors in reverse flotation are DTAB, HTAB, DTAC, and so on. On the other hand, PAM and ferric silicate were governed besides collector in order to increase activation of them. On the other hand,

Coal type	Depressant	Collector	Frother	Reference
Bituminous coal	Inorganic oxidants	Octylamine, CTAC, FAA, CTAB, CDBAC, LPC	MIBC	[29]
Subbituminous coal	Not used	DTAB	MIBC*	[45]
Bituminous & sub-bituminous coal	Dextrin	DTAB, PAM	DTAB	[94]
Bituminous & sub-bituminous coal	Dextrin	DTAB	MIBC	[46]
Sub-bituminous coal	Dextrin	DTAC	not used	[36]
Sub-bituminous coal	Dextrin	Lilaflot D817M	MIBC	[48]
Clean coal and silica mixture	Humic acids (HA)	DTAB	MIBC*	[45]
Calcite, dolomite, silica, and raw coal	Dextrin	DTAC	Not used	[35]
Quartz and clean cooking coal mixture		HTAB, HPYC		[39, 40]
Taixi oxidized coal	Dextrin	HTAB	–	[42, 95]
Quartz and clean cooking coal mixture		HPYB		[39]
Lignite coal	Not used	Aero-3477 (anionic collector), kerosene	Pine oil	[27]
Mineral pyrite	Not used	Fuel oil	MIBC	[37]
Pittsburgh coal	Not used	Fuel oil	Dowfroth 200	[37]
Mineral pyrite, coal	Not used	Fuel oil	Dowfroth 200	[48]
Quartz and clean cooking coal mixture	Dextrin	DTAB	MIBC	[39, 40]
Lignite coal	Not used	(Cationic; DDA, TTAB)	MIBC	[47]
		Anionic; SDS, non-ionic (2-ethyhexanol)/kerosene		
Lignite coal	Corn starch	DAH	MIBC	[43]
Low grade stone coal	Sodium silicate	oleic acid, EA, DDA, DC, Mixed Alimine	Terpenic oil	[70, 71]
Silica and raw coal mixture	Humic acids (HA)	DTAB	MIBC*	[25]

Table 2. Use of reagents in reverse flotation.

depressants are the reagents which are added to the pulp to make mineral surface more hydrophobic. As depressants, commonly used reagents in coal reverse flotation are dextrin, humic acids, and corn starch. Frothers are utilized for forming small size bubbles and durable forth which can bear floated minerals without getting any damage during transportation process. In reverse flotation, most common reagents are MIBC, and pine oil, terpenic oil, and

• MIBC* indicates that it was not used for all experiments	• DDA, Dodecyl amine
• TTAB, Myristyl trimethyl ammonium bromide	• HPYC, Hexadecyl pyridinium chloride
• SDS, Sodium dodecyl sulfate	• HPYB, Hexadecyl pyridinium bromide
• EA, Melamine	• CTAC, Cetyltrimethylammonium chloride
• DAH, Dodecylamine hydrochloride	• CTAB, Cetyltrimethylammonium bromide
• DC, Octadecyl amine	• CDBAC, Cetyl dimethyl benzyl ammonium chloride
• FAA, Fatty amine acetates	• Dowfroth 200, A polypropylene glycol methyl ether
• LPC, Lauryl pyridinium chloride	

Table 3. Abbreviations.

Dowfroth 200 follows it. On the other hand, the use of frothers is not compulsory for reverse flotation because some collectors possess foaming agents.

Alternatively, Yi et al., stated that waste cooking oil (WCO) can be converted into a bio-flotation agent (BFA), which can be replaced with diesel improves a new coal flotation agent with Zr-SBA-15 catalyst. Pilot program data demonstrated that WCO to BFA brings saving energy by 13%, and CO_2 emission by 76% as well as production cost when compared with petro-diesel use [96]. As a new trend, environmental aspects should be considered so that less harmful collectors should be employed within the manner of reducing the damage to environment, and in this respect, more studies should be handled to overcome environmental issues.

2.8. Conclusion

Flotation was developing at the end of 1800s, and reverse flotation was first tried in 1960s. Although not much researcher paid attention on reverse flotation issue, they contributed to literature significantly through past 50 years. With respect to these results, it is inevitable to reach success by reverse flotation.

SO_2 gases are the main triggering factor of acid rains due to propagating toxic gases after burning treatment. Sulfur gases may be found in coal in the form of organic and mineral sulfur (pyrite, marcasite, galena, and sphalerite) and sulfate (Gypsum—$CaSO_4{\cdot}2H_2O$ and Barite—$BaSO_4$). In order to restrain environment and habitat from unhealthy gases, before burning treatment of coal, they should be removed from coal. Besides, Hg and U spread to the air by burning treatment. On the other hand, minerals like Be, Cr, Ni, As, Cd, Co, Ni, Sb, Se, Pb, Co, Cl, Be, Ba, etc. may involve in water and vegetation cover and lead to great damage for habitat. These heavy minerals are also dangerous for human body because human body could not get rid of these minerals easily and cause to irreversible damages. Because of that, these minerals should be removed from coal in prior to burning treatment. Another issue about coal is about eliminating the harmful effects of CO_2, which causes greenhouse effects. To achieve this, beech trees which has great potential of consuming CO_2 gases in photosynthesis process and the habitat of artificial trees should be constituted especially in the area where coal is being consumed as a main energy source.

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Author details

Fatma Deniz Öztürk

Address all correspondence to: deniz.ozturk@dicle.edu.tr

Dicle University of Mining Engineering Department, Diyarbakır, Turkey

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