Separation of Petroleum Coke from Anode Stubs Produced During the Aluminum Electrolysis

A. Bahrami[1*], M. R. Hosseini[2], F. Kazemi[1], S. Kheiri[1], M. Bakhshi[2] and M. Rahimi[3]

*a.bahrami@urmia.ac.ir

[1] Department of Mining Engineering, Faculty of Engineering, Urmia University, Urmia, Iran.

[2] Department of Mining Engineering, Isfahan University of Technology, Isfahan, Iran.

[3] Department of Chemical Engineering, Isfahan University of Technology, Isfahan, Iran.
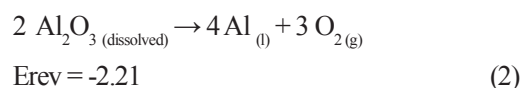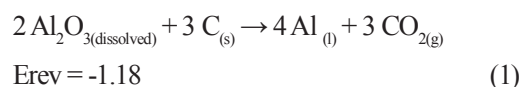
Abstract: Petroleum coke contains high amounts of carbon and is used in the manufacturing of anode electrodes for the aluminum extraction. In the process of aluminum production, some particles separate from anodes as waste which contain petroleum coke. Therefore, recycling and processing of these petroleum coke particles is the subject of this study. The ash content reduced to 31% and 13% in the jig and shaking table concentrate, respectively. These two steps were considered as the pre-processing methods and heavy media separation was used to decrease the ash content much more. Finally, flotation was performed in order to purify the particles with the size of less than one millimeter.

Keywords: Anode electrode, Gravity separation, Petroleum coke, Recycling, Flotation

1. INTRODUCTION

There are two basic technological methods for aluminum production, Prebaked and Soderberg technology. Nowadays, Hall-Heroult process is widely used for the aluminum production [1-3], and is the only industrial way of aluminum production [2]. This process was developed by Charles Martin Hall [4], and Paul Louis Heroult [5], independently. Electrochemical decomposition of aluminum oxide (Al_2O_3) is the basis of this process. In Hall-Heroult electrolysis cells, prebaked carbon anodes which weight as much as 1250 kg and approximately have a working face size of 0.70 by 1.25 m and 0.5 m height [6] are used in the primary aluminum production [7-9]. These two equations [2] show the reactions in the Hall-Heroult process:

$$2\,Al_2O_{3(dissolved)} + 3\,C_{(s)} \rightarrow 4\,Al_{(l)} + 3\,CO_{2(g)}$$

$$Erev = -1.18 \tag{1}$$

$$2\,Al_2O_{3\,(dissolved)} \rightarrow 4\,Al_{(l)} + 3\,O_{2\,(g)}$$

$$Erev = -2.21 \tag{2}$$

The over-potential of anodes can be as high as 0.6 V [10]. The amount of main raw materials needed for the production of one ton aluminum metal is estimated approximately as aluminum oxide, 2.0 ton; carbon, 500 kg; aluminum fluoride, 20 kg. Moreover, 13.5 kWh electrical energy is required [2]. Prebaked and Soderberg anodes are the anode designs which are currently in use (Table 1) [3-6].

Table 1. World aluminum production and carbon requirements

	MM tons 2008	MM tons 2020
Aluminum	38	68
Anodes	21	28
Cathodes	0.26	0.41
Green/calcined coke	20.14	35.27
Coal tar pitch	4	7

The carbon electrodes are the source of necessary reactions, e.g. in the reduction of alumina to aluminum and also used for transmitting power to electro-thermal processes [11]. The heart of an aluminum electrolysis cell is the carbon anode [12]. Anodes are produced by baking the composition of coal tar pitch binder [8, 13], because of their excellent binding properties [14] and high carbon content [1], recyclables [8, 9, 13], and calcined petroleum coke (PC) [8, 9, 13, 15] which is the main raw material [9, 14, 16-18]. The amounts of these general materials were reported as 14-17%, 15-30%, and 50-65% [3] or 13-15%, 20-30%, and 55-65% [8], respectively. In another research, it was mentioned that the anodes are included PC (60-70 wt.%), coal tar pitch (14-17 wt.%), and anode scrap (15-20 wt.%) [19].

During the aluminum electrolysis, some anode particles separate from the anodes called anode stubs. These stubs could be used as raw material in the production of new anodes [3]. The theoretical minimum anode consumption is 0.33 kg of carbon per kilogram of aluminum [6]. The PC purity is very important in carbon anode production because of the significant effect of carbon anode in the aluminum electrolysis [17], also energy efficiency and productivity of smelting cells are affected by the physical quality of the anodes [6]. The prebaked anodes have to be replaced by new anodes after 20-30 days [2]. The used anodes are recyclable which can account for 15-30% of the mass used in green anode make-up [6].

PC is a byproduct of oil refining industry [16, 20] which has a low cost and high calorific value [20], it also accounts for 15-20% of the total cost of aluminum electrolysis production [18]. About 25% of all raw coke is calcined worldwide, and approximately 70% of all calcined coke is used in aluminum production [6], PC is black-colored and may contain limited amounts of metals, sulfur and non-volatile inorganic compounds [16]. PC includes carbon (about 85-92% [21]), hydrogen, oxygen, nitrogen, sulfur, and ash (including heavy metals such as vanadium and nickel) and also has economic value as both a raw material and heating fuel [16]. It is not toxic, non-reactive, and stable at ambient environment conditions, and has a low potential to affect terrestrial or aquatic environments [16]. In electrode and aluminum industry, the quality of coke is basically dependent on the content of sulfur, ash, volatiles, moisture, and metals. Furthermore, its granulometric composition, actual density, and electrical resistivity are other important factors [22].

In accordance with a study by Sredniawa (in polish), different methods such as jigging, flotation, and classification are more economical than other methods to remove PC's associated ash and pyrite [21]. There are many studies involving the recovery of fine-sized petroleum coke from lime calcination plan tailing [24, 25, 26, 27-28]. In these studies mostly flotation was chosen as a separation method depending on hydrophobic surface characteristics of petro coke. Also, there are several different reports in the literature about the extraction of different materials from the anode stubs. The recycling of PC from anode stubs has been never reported yet. Therefore, in this research, by performing different processing tests on experimental and pilot scale, we try to determine the most efficient method for the recovery of anodes.

In the recent study, a novel approach is reported for the recovery of PC from anode stubs using jigging, shaking table, heavy media separation, flotation, and magnetic methods. Finally, according to the results of the study, an initial PC concentration circuit is put forward.

2. MATERIALS AND METHODS

2. 1. Materials

Samples (10 metric ton) were collected from different parts of a scrap aluminum recovery plant depot, in order to perform the experiments and the pilot tests. After proper mixing and considering the principles of sampling, 20 samples (each 1 kg) and 5 samples (each 50 kg) were collected for the experimental and the pilot tests.

2. 2. Sieve Analysis

To obtain the size distribution of the samples, sieve series was used according to the ASTM standard. In this series, sieves with aperture sizes of 12.7 mm and 0.106 mm were chosen as first and the last ones, respectively. Three one-

30

kg samples were used for the sieve analysis and the grain size distribution was shown in Table 2. In addition, ash and fixed carbon content were determined for each size fraction using CHNS/O Analyzer. To determine the amount of ash content, a sample from each grinding fraction و powdered. Then, samples burned in a laboratory furnace for 90 minutes at temperature 700 ˚C. During this process, the carbon burnt and left the reminders. The results are shown in Table 2.

2. 3. Jigging

A jig laboratory scale equipment manufactured by Denver Company was used for jigging tests (Model of Jig: Hartz and Dimensions of the Jig Bed: 100×70 mm). PC placed on the bed, and an oscillatory motion of water was created in the layers. The oscillation frequency was set to a degree so that in each cycle the PC particles would not reach the terminal velocity. Therefore, heavy particles were gradually separated from the light particles within a short time. This test was performed to reduce ash particles larger than 2 mm. The oscillations and water flow were set to 150 min^{-1} and 4 L/min, respectively.

2. 4. Shaking Table

This test was performed on an industrial scale using a Wilfley shaking table device (Dimensions of table: 64×129 cm). 50 kg samples with the dimensions of 1-4.75 mm were used in this test. After some preliminary tests, table optimum condition was determined as the slope of 5 degrees, solid percentage: 25-30%, water flow: 10 l/min, and the number of oscillations was set to 150 min^{-1}.

2. 5. Heavy Media Separation

Heavy media separation was used for indexing coarse PC particles (+1 mm). For this purpose, heavy media tests were applied on two different fractions, 1-4.75mm, and +4.75mm. In this method, four heavy media with the density of 1300, 1500, 1700, and 1900 kg/m^3 were prepared using zinc chloride. Density evaluation was performed using a hydrometer (accuracy 100 kg/cm^3). PC samples with the weights of less than 10 kg were placed in the washing basket and then placed in a bath containing the first heavy liquid with the density of 1300 kg/m^3. After vertical shaking of the basket for releasing all of the particles, these materials were given enough time to float or sink. In accordance with the range of sample size, this separation time was between 1 to 5 minutes. More time is needed if the PC particles are finer. The floated materials were separated using a shovel and then was left to drip for separating the liquid from the sample. The washing basket in which the materials have settled was placed in the second bath with the density of 1500 kg/m^3. In this section, 1300-1500 kg/m^3 PC was obtained. Similarly, the basket was placed in the next baths and the floating section in each specific gravity was separated. In the last bath, in addition to the floating material in 1900 kg/m^3, the settled material was placed in their own strainer. This process was repeated

Table 2. Results of the sieve analysis

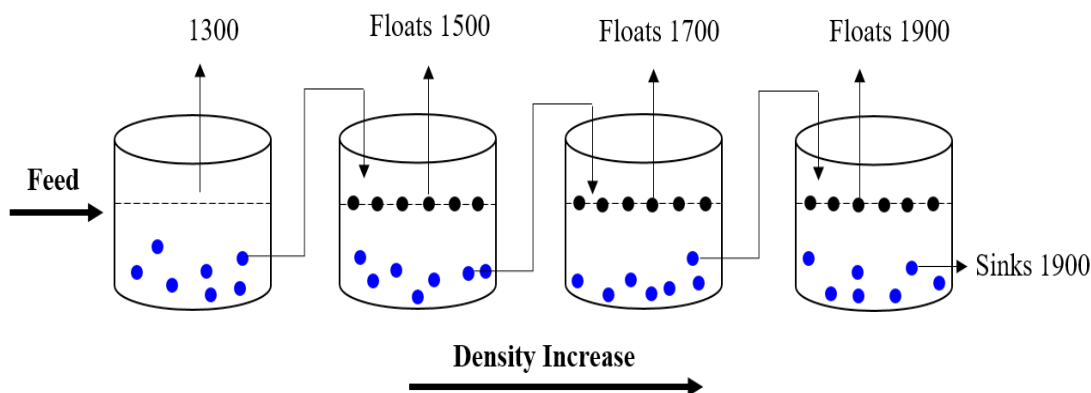| Mesh	Nominal aperture size (mm)	Oversize (wt. %)	Cumulative Oversize (wt. %)	Cumulative undersize (wt. %)	Ash (%)	Carbon (%)
+1.2	+12.7	9.61	9.61	90.39	40.84	30.67
+4 -1.2	+4.75 -12.7	31.77	41.38	58.62		
+10 -4	+2 -4.75	44.23	85.61	14.39	39.08	47.87
+18 -10	+1 -2	6.45	92.06	7.94		
+30 -18	+0.6 -1	0.85	92.91	7.09	35.97	52.82
+45 -30	+0.355 -0.6	0.85	93.76	6.24	28.75	57.97
+140 -45	+0.106 -0.355	1.45	95.21	4.79	42.64	45.93
-140	-0.106	4.78	100	0	59.03	24.38

Fig. 1. Heavy media separation experiments

until all the samples in the heavy liquids turned out to be washed. The float and sink parts were dried, weighed and prepared for the ash and fixed carbon analyses. This process was shown in Fig. 1.

2. 6. Flotation

The floatation tests were conducted in Denver cells (each 2 L) at various agitation speeds and 25% solid content for particles less than 1 mm. In these experiments, gas oil, and MIBC were used as collector and frother, respectively. Two minutes of preparation and mixing time before the chemical addition was considered in the experiments. After adding collector and frother, 2 and 1 min was considered as the preparation time, respectively. The rotation speed of impeller was set to 1200, 1650, and 1000 rpm for 1, 2, and 3 concentrates.

2. 7. Magnetic Separators

The observation of the samples showed that the sample contained iron particles, so a low-intensity magnetic separator about 1000 gauss was used in order to remove iron particles from PC samples, regardless of the size distribution.

3. RESULTS AND DISCUSSION

3. 1. Sieve Analysis

Due to the similarities of PC and coal in appearance and physical properties, the first stage to identify the sample and possible options for mineral processing was the determination of grain size distribution, the amount of ash and fix carbon in different fractions. Sieve analysis is one of the most common tests for the measurement of the particles size, and because of the ease of use and the ability to measure a wide range of particles is used by the processing industry. As shown in Fig. 2, the d80 equals to 10.6 mm and about 8% of the particles are less than 1 mm. In addition, about 10% of the particles are greater than 12 mm. As it comes from Table 2, the amount of carbon increases with the decrease of the particles size to 0.355 mm, and most of the ash is related to the particles coarser than 12.7 mm. It should be noted that the following factors can be used to justify the changes of the ash percentage:

● Difference in the hardness of the non-carbon and carbon materials causes the concentration of waste materials in the coarse parts while carbon materials move to the fine fractions due to its softness.

● The involvement of waste material with coal is another reason for the high content of ash in coarse fraction. The smaller the particle size the less this effect.
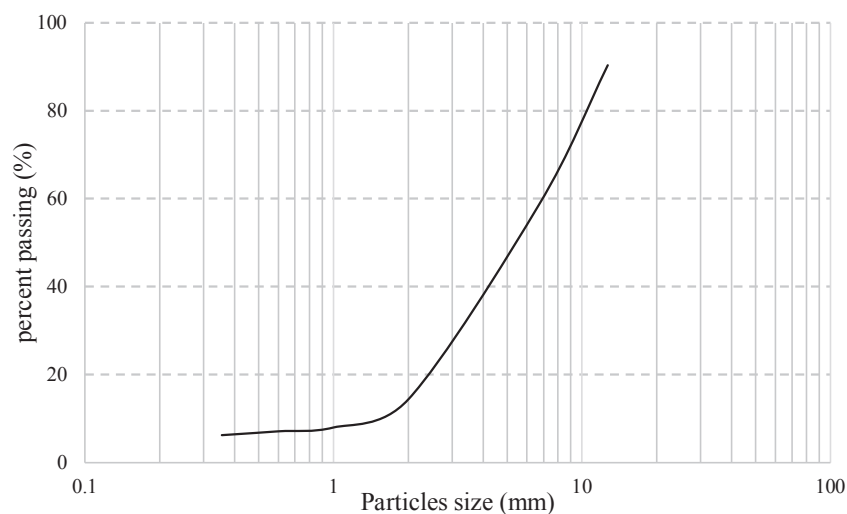
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Fig. 2- Size distribution of PC
Fig. 2. Size distribution of PC

3. 2. Jigging

The results of the jigging test are presented in Table 3. These results show that the greater the particle size, the higher the waste and the ash content. For particles with a dimension of more than 4.75 mm, the ash percent increased. In this size range, the carbon grade of the concentrate was about 69%. Generally, the finer grain size in jigging machine is almost under the influence of upward water flow and separation does not occur effectively.

According to the results, the use of this machine could be effective as a prearranged step to reduce the ash without any effect on recovery. Afterwards, the obtained concentrate can be further processed using another method to reach the desired product.

The jigging experiments were performed using the rest of the size fractions; however, no concentrate was produced. For making an accurate decision about this device, an industrial scale test is suggested. Generally, according to the carbon grade in concentrate and ash grade in waste, it can be said that this step is useful for +4.75 mm particles.

3. 3. Shaking Table

Three products including concentrate, middling, and tailing were obtained from this test. The results are shown in Table 4. The shaking table experiments showed promising results. If the table surface is bigger, the particles have enough time to classify into their correct positions. So by precise adjustment of product withdrawal location on the deck, better results could be obtained. Another benefit of using shaking table is the good quality of the tailing. The low recovery in shaking table experiments refers to the presence

Table 3. Results of the jigging experiments

Size	Feed Ash	Water flow	Jig speed	Concentrate		Tailings	
mm	%	ml/s	rpm	Wt (%)	(%) Ash	Wt (%)	(%) Ash
+2-4.75	86.1	24.1	600	49.8	15.2	50.2	90
+4.75-12.5	61.5	32.5	719	44.9	47.2	55.7	94.1
+4.75	57.8	29.9	812	35.3	31.1	64.7	94.2
+12.5	62.9	35.1	850	15.2	31.7	84.8	75

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of intermediate product in this technique. The experiments showed that the intermediate product could be mixed with the feed and arranged again in a continuous system to reach the desired recovery. They could be mixed together because the ash contents of the feed (26%) and middling (20%) are almost close to each other. This technique could also be used to remove the major part of the waste of the initial feed so that the desired product could be produced in the next steps using other methods of processing.

3. 4. Heavy Media Separation

Due to the lack of float samples in liquids with a specific gravity of 1300 kg/m³, this fraction was waived. As shown in Table 5, 3.39% of the +4.75 mm particles were floated in 1500 kg/m³ which contained 99% of carbon, and also by adding the sunken materials of this section in the 1700 kg/m³ solution, 20.25% of these materials were floated

which was contained 98% carbon and less than 2% ash. In the 1900 kg/m³ solution, 4.85% of the particles were floated which contained 88.5% carbon. The other materials (71.51%) which were sunken, only contained 1.35% carbon and the rest were ash and different impurities.

Table 6 presents the result of the dense medium test on +1-4.75 size fraction. As it stands, float particles in 1500 kg/m³ solution were 3.12% of the total weight which this content for 1700 kg/m³ solution increased up to 19.79%. Carbon content in these two fractions was more than 98%. In the 1900 kg/m³ solution, 14.31% of the particles were floated and generally, 62.78% of the materials were sunken which contained 89.15% ash. In accordance with the graphs illustrated in Fig. 3 and Fig. 4, the specific gravity of the required dense media for obtaining a low ash concentrate (less than 4% ash) and the recovery can be obtained. Results are presented in Table 7.

Table 4. Results of the shaking table test

Product type	Recovery	Ash (%)	Wt (%)
Final concentrate	47	13	33
Middle product	25	26	21
Tailing	-	78	46

Table 5. Result of the float and sink analysis (on +4.75 mm size fraction)

Specific gravity	Floats weight (%)	Cumulative float (Wt %)	Cumulative sink (Wt %)	Carbon (%)	Ash (%)
- 1500 +1300	3.39	3.39	96.61	99	1>
- 1700 +1500	20.25	23.64	76.36	98	2>
- 1900 +1700	4.85	28.49	71.51	88.5	6.56
+1900	71.51	100	0	1.35	89.72

Table 6. Result of the float and sink analysis (on +1-4.75 mm size fraction)

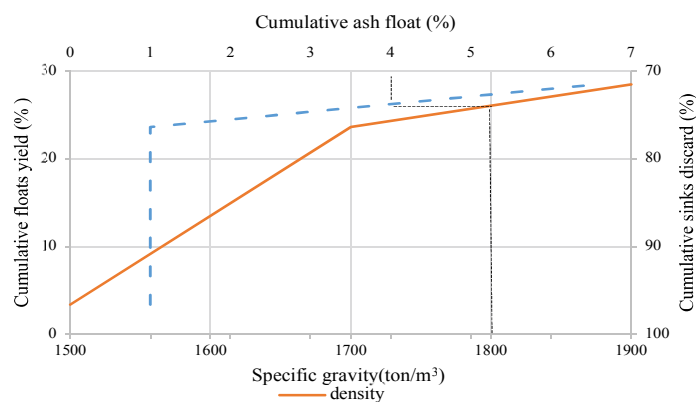| Specific gravity	Floats weight (%)	Cumulative float (Wt %)	Cumulative sink (Wt %)	Carbon (%)	Ash (%)
- 1500 +1300	3.12	3.12	96.88	99	<1
- 1700 +1500	19.79	22.91	77.09	98	<2
- 1900 +1700	14.31	37.22	62.78	90.51	4.15
+1900	62.78	100	0	0.39	89.15

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Fig. 3. Washability curve of the PC sample (+4.75 mm particles)
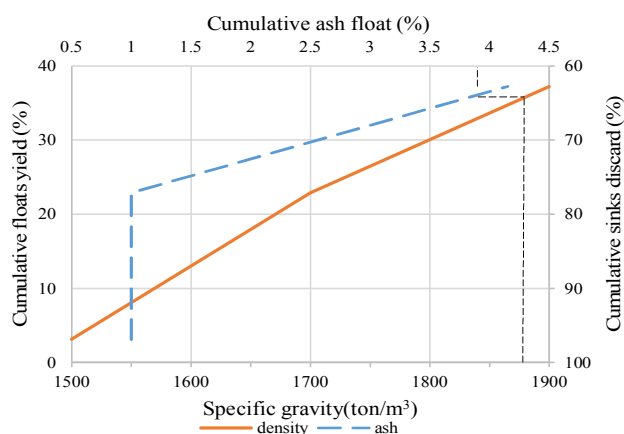

Fig. 4. Washability curve of the PC sample (+1-4.75 mm particles)

Table 7. The optimum conditions of heavy media separation

Size (μm)	Separation density (g/cm³)	Concentrate (wt %)	Concentrate ash (%)
+4.75	1.8	26	>4
+1، -4.75	1.89	36	>4

Regarding the low ash of the floated part of the 1800 kg/m³ solution, gravity separators can be used to reduce large amounts of waste in the sample as prearranged devices. In PC, materials with the density of more than 1900 kg/m³ are tailings. Finally, it can be said that dense media method is suggested as a suitable solution to bring the ash contents of the PC to the desired level. Although this method is more expensive than the other gravity methods and needs specific and detailed controls, it can be used instead of other gravity techniques when they fail to provide the intended purpose.

The function of gravity separation devices (for example jig) is investigated by using distribution curves. Determining the distribution curves for controlling gravity separation processes is important and can provide a proper correction for controlling a given process, and it is possible to simulate and predict the results [29]. The distribution curve is obtained by computing the distribution coefficient by the average density in each section. In order to plot the distribution curve, weighting the concentration of concentrate and sink - float tests for concentrate and tailings

3. 7. Designing the Initial Processing Circuit

Using gravity methods like dense media separation, jigging, and shaking table, different experiments were conducted to reduce the PC ash contents. In dense media separation, the ash content reduced to 4% for particles greater than 1 mm. The results of the jigging tests represent that jigging is useful as a pre-concentration step which makes the recovery of PC possible with the ash content of less than 31%. In addition, in the shaking table experiment, the ash content of the final concentrate was 13%. In this case, if the table works continuously in a circuit and the intermediate product is sent back to the table feed, the recovery will be increased. Considering the results, this method is useful for particle size ranging between 1 to 4.75 mm. Floatation was carried out for particle size fraction less than 1 mm. The results of the floatation tests were not acceptable because of the low recovery and high ash content of the concentrate. In fact, a great deal of valuable material was transported to the tailings. But probably this method is favorable for -1 mm particles and has ability good potential for re-examination. Also, magnetic separation tests were conducted without considering the particles range. Thus, according to the results of these experiments, a circuit was proposed to reduce the ash content of the PC and illustrated in Fig 6.
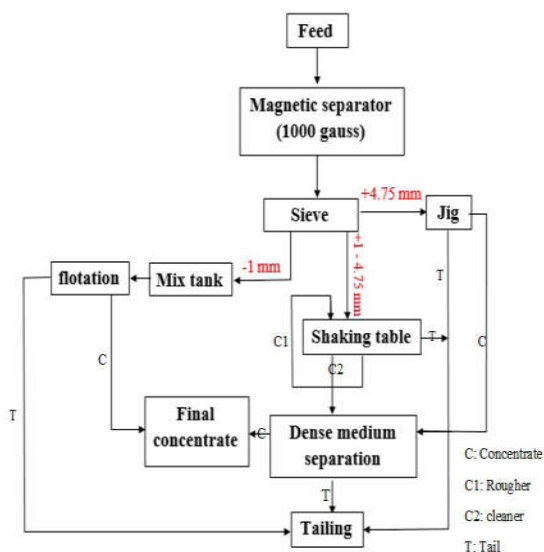

Fig. 6. The proposed circuit for the recovery of PC

4. CONCLUSION

Anode stubs of aluminum factories were examined and underwent different processing methods. Shaking table and jigging were proposed as pre-processing steps. Also, heavy media separation was considered as the final concentration method to obtain a product with minimum ash content. Flotation as the only approach to purify the particles less than 1 mm was also examined, and the results indicated that regrinding of the feed was necessary to improve the flotation efficiency. Finally, using the outcomes of the concentration tests, an initial circuit was proposed for the PC recovery.

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