Research Article

Characterization of Glasses in One Type of Alumina Rich Fly Ash by Chemical Digestion Methods: Implications for Alumina Extraction

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In recent years, one type of alumina rich fly ash (ARFA) with about 50 wt% of alumina has been extensively investigated for alumina extraction in China. Due to the silica in ARFA, alumina extraction would have to generate a huge amount of solid waste. There is a growing interest in the glasses in ARFA, because they are composed mainly of silica and could be removed prior to alumina extraction. In this work, the glasses in ARFA have been investigated by chemical methods, that is, acid and base digestions. The chemical compositions have been measured by XRF for ARFA from the digestion processes. The K_2O standard, XRD, and FTIR spectroscopies were successfully used to define the digestions processes, and size analysis and SEM-EDX provided rich information on particle transformations. As a result, acid and base digestion methods were found to produce very similar results for the glasses in ARFA. The K_2O standard was attributed to the formation of glasses by illites, and TiO_2 and Fe_2O_3 were proposed to originate from ilmenite in alumina rich coals (ARC). Some implications of the results were also discussed for the alumina extraction from ARFA.

1. Introduction

China's alumina industry relies heavily on foreign bauxite, which accounts for more than 60% of its total consumption, according to China Industry Security Guide. It has been found that the coal deposits in the Midwest of Inner Mongolia Autonomous Region and North Shanxi Province of China are rich in alumina [1, 2]. After burning alumina rich coal (ARC) for power generation, a huge amount of alumina rich fly ash (ARFA) has been produced, and routinely buried deep in ground or piled up in open fields, causing serious environment problems [1–4]. The ARFA occurs with about 50 wt% of alumina favorable for alumina extraction, as well as about 40 wt% of silica. Besides, about 10–30 billion tons of ARFA would be produced in these regions.

Recently, a comprehensive review of alumina extraction from fly ash has been published with a focus on China [1]. For the promising sintering methods, a large amount of lime

has to be added to react with silica for the formation of solid wastes like $2CaO \cdot SiO_2$, so that alumina could be extracted. As a result, even more waste is produced than the alumina extracted. For the ARFA, silica occurs mainly in glassy state or as part of mullite [2–4]. Hot dilute caustic solutions readily dissolve silica in glassy state, and predesilication should be preferably performed for ARFA prior to alumina extraction. Predesilication reduces silica in ARFA, lime addition would accordingly be decreased, and so does the waste production [1–4].

Glasses in fly ash have attracted much attention for a long time. In the early days [5], researchers became interested in the glasses because they affect the stability of fly ash added in cement. The natural weathering of fly ash proceeds with the dissolution of glasses [6], and the glasses provide predominant component of dissolved iron in the open ocean [7]. A variety of zeolites have been synthesized by dissolving the glasses for applications like ion exchange, gas adsorption,

and water adsorption [8–11]. More recently, the dissolved glasses have been used to produce ultra-clear glass [3], white carbon black and active calcium silicate [12].

In this work, the concern is the amount and nature of glasses in ARFA, because it could set the predesilication limit for alumina extraction from ARFA. Generally, two groups of methods have been developed for the study of glasses in fly ashes [5], that is, spectroscopic methods like XRD and chemical methods like acid and base digestions. Despite the great progress in quantifying the glasses in fly ashes [13–16], the XRD has been generally regarded as a semiquantitative tool, due to inherent variability of a number of crystal frameworks, sample preparation, grain-size effects, preferred orientation, and absorption of X-rays by other components. Other spectroscopic techniques like NMR, FTIR, and Raman have been known to mainly yield qualitative information on the chemical compositions of the glasses in fly ash [2, 5]. The chemical methods highlight acid (HF) and base (NaOH) digestions of glasses in fly ashes. Dilute HF solutions have been known to rapidly digest the glasses in fly ashes, and the process could be readily traced [17–19]. For NaOH solution digestion of glasses in fly ashes, three steps should be involved, that is, step Base Dissolution I, step Acid Dissolution (HCl), and step Base Dissolution II [2]. It seems that the glasses in ARFA can be effectively characterized by utilizing chemical methods corroborated by spectroscopic techniques.

2. Experimental

2.1. Procedures for Acid and Base Digestions of ARFA

2.1.1. Acid Digestion of ARFA. The ARFA samples have been taken from one of Shenhua Group's power plants. A weighted ARFA sample of 10.0 g was added to a 1.0 wt% HF solution of 1000 mL at the ambient temperatures of $20 \pm 1^\circ\text{C}$, and the solution was stirred for a predetermined interval. Then, the solution was filtered and washed to obtain the sample of acid digestion ARFA. Since 1.0 wt% HF solution has been known to easily digest the glasses in fly ashes [17–19], the first interval was set at 15 min, and other intervals were 1 hr, 2 hr, 4 hr, 8 hr, 16 hr, and 32 hr. All acid digestion ARFA samples were dried at 120°C overnight for analysis.

2.1.2. Base Digestion of ARFA. This method involves three steps, and it is claimed that the glasses in ARFA would be totally removed through the procedures [2]. Step Base Dissolution I: a weighted ARFA sample of 40.0 g was added in a 30.0 wt% base solution prepared by dissolving 20.0 g NaOH and was allowed to react at 95°C for 4 hr prior to filtering and washing. The cake was dried at 120°C overnight for analysis. Step Acid Dissolution: the cake prepared in the step Base Dissolution I was transferred into a 15.0 wt% HCl solution of 80 mL. The slurry was allowed to react at 80°C for 1 hr prior to filtering and washing, and the cake was dried at 120°C overnight for analysis. Step Base Dissolution II: the cake prepared by going through the steps Base Dissolution I and Acid Dissolution was further treated precisely as Step Base Dissolution I.

2.2. Characterization and Measurement of ARFA Samples. XRF (ZSX Primus II), XRD (RINT 2000), and FTIR (Nicolet Nexus) measurements were applied for the dried ARFA from acid and base digestion processes. Particle transformations of ARFA in digestion processes were investigated by SEM-EDX (S4800-EMAX) and size analysis (Mastersizer 3000).

3. Results and Discussion

3.1. Chemical Compositions and Weights of ARFA in Acid and Base Digestion Processes. The weight percentage changes of ARFA are shown in Figure 1 for acid and base digestion processes. In Figure 1(a) for acid digestion process, the weight of ARFA decreases rapidly in the beginning and even within 15 min over 20 wt% is lost into the HF solution. The rate of weight loss then slows down and decreases linearly till the interval of 4 hr with a loss of 38.1 wt%. After that, the rate of weight loss becomes increasingly slower, and 55.9 wt% of ARFA is lost in the interval of 32 hr. In Figure 1(b) for base digestion process (0–4 hr: step Base Dissolution I, 4–5 hr: step Acid Dissolution, and 5–9 hr: step Base Dissolution I), the weight of ARFA decreases faster in step Acid Dissolution, and 40.2 wt% of ARFA is finally lost after step Base Dissolution II.

Chemical compositions of acid and base digestion ARFA measured by XRF are given in Figure 2, and only major components in the form of stable oxides with contents higher than 1 wt% are presented, such as SiO_2 , Al_2O_3 , CaO , TiO_2 , and Fe_2O_3 . In addition, K_2O is also given in Figure 2, because it may serve as an indicator for glass digestion. Figure 2 is intended only to provide an illustration of chemical compositions of ARFA after digestions, and the patterns should not be quantitatively related to the trends of component dissolution.

3.2. Identification of Glasses in ARFA in Acid and Base Digestion Processes. It has been generally agreed that chemical digestions can dissolve glasses as well as other phases in fly ashes, depending on the conditions [2, 19]. In this section, K_2O standard, XRD, FTIR, SEM, and size analysis have been used to characterize ARFA in acid and base digestion processes, and based upon the results the glasses have been clearly identified from other components in ARFA.

3.2.1. K_2O Standard. With the exhaustive experiments, it has been found that “the completion of removal of the potassium could serve as a maker for completion of dissolution of the glass phase in the fly ash” [19]. According to the weight percentages of acid digestion ARFA in Figure 1(a) and the weight percentages of K_2O in acid digestion ARFA in Figure 2(a), the absolute weights of K_2O in acid digestion ARFA can be conveniently calculated. In Figure 3, K_2O in acid digestion ARFA has been given in weight percentage of total K_2O in raw ARFA as a function of acid digestion time, and there is still 5 wt% K_2O retained even in the interval of 32 hr. The remaining K_2O probably occurs in some forms that cannot be easily attacked by acid, for example, contained or buried as impurities in mullite and corundum crystals. Therefore, once K_2O becomes stable in ARFA samples in given intervals, the glasses could be regarded as completely dissolved or digested.

FIGURE 1: Weight changes of ARFA in acid (a) and base (b) digestion processes.

FIGURE 2: Chemical composition changes of ARFA by XRF in acid (a) and base (b) digestion processes.

In Figure 3, it is apparent that K₂O in acid digestion process becomes stable at the interval of 8 hr. However, there is also the possibility of achieving a stable K₂O at an earlier time than the interval of 8 hr. Such time could be estimated by drawing a line through K₂O masses at intervals 2 hr and 4 hr to cross the line for K₂O of 5 wt%, and it is determined to be 6.2 hr. Therefore, the complete removal of K₂O may occur at 6.2–8 hr in acid digestion process. According to Figure 1(a), 41.6 wt% and 44.3 wt% of ARFA were lost at 6.2 hr and 8 hr

in acid digestion process, which should be set as the lower and upper limits of glasses in ARFA. If the average is taken, the completion of glass digestion may occur at 7.1 hr with a loss of 42.9 wt%. By contrast, according to Figure 1(b) for base digestion process, about 40.2 wt% of ARFA was lost in the base digestion time of 9 hr after step Base Dissolution II, which has been taken as the glass content [2]. Therefore, the glass content measured by base digestion process is about 2.7 wt% lower than acid digestion process.

FIGURE 3: K₂O in ARFA from acid digestion process.

In the study by quantitative XRD spectroscopy of 75 European fly ashes, a wide range of glass contents from 45 wt% to 90 wt% have been calculated [16], and low alkali oxides were found not to support high glass contents. The alkali oxides are mainly K₂O of 0.46 wt% in ARFA, and therefore, even lower glass content of 40.2–42.9 wt% has been reported in this work by acid and base digestions. It should be noted that the glass contents in ARFA were among the lowest according to the literature survey [5, 13–16].

3.2.2. XRD Spectroscopy. In Figure 4(a), the XRD spectra in the 2θ range of 10–60° are given for acid digestion ARFA, as well as raw ARFA. In raw ARFA, major crystal phases are mullite and corundum. The weak peak with 2θ at 29.3° may be ascribed to ferrite spinel, which has been dissolved even in 15 min [19–21]. The broad band in the 2θ range of 15–30° has been previously linked with the glasses in fly ashes [2, 5], which have also been dissolved in 15 min. In the XRD spectra of 32 hr, a new peak with 2θ at 29.0° might be attributed to CaF₂ crystal formed in extended period of time [22]. In Figure 4(b), the broad band is enlarged to display the glasses digestion of ARFA. The broad band of glasses is disappearing from 15 min to 8 hr, after which it becomes almost flat till 32 hr, which is in good agreement with the K₂O standard.

In Figures 5(a) and 5(b), the XRD spectra in the same 2θ ranges are given for base digestion of ARFA, as well as raw ARFA. The peak for ferrite spinel remains, though greatly weakened, after step Base Dissolution I and disappears totally when step Acid Dissolution is applied. It seems that ferrite spinel is more resistant to base than acid digestion. The broad band of glasses becomes increasingly flat with the progress of base digestion process, and the small peaks for crystalline silica disappear after step Base Dissolution I. A new peak with 2θ at 24.4° appears after step Base Dissolution I, disappears when step Acid Dissolution is applied, and reappears with a

FIGURE 4: The XRD spectra of ARFA from acid digestion process, (a) in the 2θ range of 10–60° and (b) in the enlarged 2θ range of 15–30°. Note that the spectra in (a) have been offset for clarity and the spectra in (b) are given without treatments.

slightly different 2θ at 24.6° after step Base Dissolution II. The peak has been previously attributed to hydroxysodalite [10]. Hydroxysodalite formation in step Base Dissolution I blocked glass digestion, and step Acid Dissolution was applied to destroy it, so that glasses could be completely digested by step Base Dissolution II [2]. But from the XRD spectra for step Base Dissolution II, hydroxysodalite still occurs to cover the ARFA. This could explain why acid digests more glasses (2.7 wt%) than base.

3.2.3. FTIR Spectroscopy. In Figure 6(a) for the FTIR spectra of acid digestion ARFA and raw ARFA, the three peaks at 563 cm⁻¹, 740 cm⁻¹, and 875 cm⁻¹ seem stationary and get increasingly shaped with the progress of acid digestion. Therefore, the three peaks should represent the acid-resistant components of ARFA and are attributed mainly to mullite

FIGURE 5: The XRD spectra of ARFA from base digestion process, (a) in the 2θ range of $10\text{--}60^\circ$ and (b) in the enlarged 2θ range of $15\text{--}30^\circ$. Note that the spectra in (a) have been offset for clarity and the spectra in (b) are given without treatments.

FIGURE 6: The FTIR spectra of ARFA from acid (a) and base (b) digestion processes. Note that the spectra in (a) and (b) have been offset for clarity.

[23]. By contrast, as acid digestion proceeds from 0 hr to 8 hr, the peak at 460 cm^{-1} moves to 440 cm^{-1} , and the peaks at 1095 cm^{-1} and 1160 cm^{-1} move to 1135 cm^{-1} and 1170 cm^{-1} , respectively. The band at around 450 cm^{-1} has been assigned to the O-Si-O bending vibration and will red-shift as the matrix becomes increasingly polymerized (3D, sheets). The bands at around 1150 cm^{-1} have been attributed to Si-O stretching vibration and will blue-shift as the matrix gets increasingly polymerized (3D, sheets) [5, 19, 23]. The glasses in fly ashes are known to represent a depolymerized matrix (chain, sheets). Therefore, the red-shift from 460 cm^{-1} to 440 cm^{-1} and the blue-shifts from 1095 cm^{-1} to 1135 cm^{-1} and

from 1160 cm^{-1} to 1170 cm^{-1} should correspond to glasses digestion of ARFA. As acid digestion proceeds further to 16 hr and 32 hr, all the peaks present no changes in their positions and can be roughly assigned to mullite [23].

In Figure 6(b) for the FTIR spectra of base digestion process, similar observations can also be made. With the progress of base digestion, the three peaks at 563 cm^{-1} , 740 cm^{-1} , and 875 cm^{-1} do not change very much and should correspond to the base-resistant components comprised mainly of mullite. Even after step Base Dissolution I, the peak at 460 cm^{-1} has moved to 440 cm^{-1} and the peaks at 1095 cm^{-1} and 1160 cm^{-1} have moved to 1135 cm^{-1} and

FIGURE 7: Particle transformations in acid (a) and base (b) digestion processes.

1170 cm^{-1} , respectively. This means the glasses in ARFA may have been largely digested, but there is a new peak appearing at around 990 cm^{-1} , which can be assigned to hydroxysodalite according to previous studies of zeolite synthesis from coal ash [24]. Hydroxysodalite forms by dissolved silica and alumina in step Base Dissolution I and can be destroyed by acid. In step Acid Dissolution, hydroxysodalite was totally removed, as substantiated by the disappearance of the peak at around 990 cm^{-1} . In step Base Dissolution II to digest the glasses in ARFA, the peak assigned to hydroxysodalite appears once again, though greatly weakened. Therefore, the glasses obtained by base digestion would be underestimated.

3.2.4. Size Analysis. Though the morphologies of fly ashes have been extensively investigated by SEM and TEM, revealing interesting features like cenosphere and plerosphere [5, 12, 25], the information on particle transformations has rarely been reported. In this work, to define acid and base digestion processes, the size distributions of ARFA samples have been measured, and the results are given in Figure 7.

In Figure 7(a), the size distributions for acid digestion ARFA and raw ARFA have been plotted for comparison. The main peak for raw ARFA occurs at $96\text{ }\mu\text{m}$, and after 15 min and 1 hr in acid digestion process, it moves to $108\text{ }\mu\text{m}$ and $112\text{ }\mu\text{m}$. This means medium size particles tend to be digested in the beginning. When acid digestion proceeds to 2 hr, the main peak breaks into two parts, one at $86\text{ }\mu\text{m}$ and the other at $20\text{ }\mu\text{m}$, and many large particles could have collapsed in this moment. When acid digestion proceeds further to 4 hr, 8 hr, 16 hr, and 32 hr, the general shapes of size distribution do not change much, but they follow a trend of decreasing the main peaks to $76\text{ }\mu\text{m}$, $54\text{ }\mu\text{m}$, $34\text{ }\mu\text{m}$, and $26\text{ }\mu\text{m}$. In Figure 1(a), the

weight loss also decreases to large extent in this period. This means the structures of ARFA become rigid, and digestion occurs by etching the outer layers of particles. Generally, there are two small peaks at $0.8\text{ }\mu\text{m}$ and $2.3\text{ }\mu\text{m}$ in different acid digestion ARFA, which may be ascribed to acid-resistant building pieces of ARFA. The building pieces occur in very small amounts in raw ARFA and accumulate rapidly as ARFA is disintegrated in acid digestion process.

In Figure 7(b), the size distributions for base digestion ARFA and raw ARFA have been plotted for comparison. Even with step Base Dissolution I, the main peak has moved from $96\text{ }\mu\text{m}$ in raw ARFA to $48\text{ }\mu\text{m}$. At the same time, the two small peaks at $0.8\text{ }\mu\text{m}$ and $2.3\text{ }\mu\text{m}$ grow considerably. But with step Acid Dissolution, the position of main peak decreases only slightly to $42\text{ }\mu\text{m}$, and the two small peaks display some shrinkage instead of expansion, which means some building pieces could have been digested by step Acid Dissolution. With step Base Dissolution II, the position of main peak shifts further slightly to $38\text{ }\mu\text{m}$, and the two small peaks grow greatly, which probably means the production of enormous building pieces.

Acid and base digestions are very different in the mechanisms, side reactions, and products. Besides, acid digestion was carried out under mild conditions, and base digestion was performed at high temperatures and with high NaOH concentrations. As a result, the size distributions cannot be reproduced. Nevertheless, the building pieces of ARFA have been consistently identified by two digestion methods.

3.2.5. SEM-EDX. In many SEM pictures for disintegrated ARFA from acid and base digestions, acicular crystals have been frequently observed to have diameters of less than

FIGURE 8: The SEM picture of building pieces in disintegrated ARFA. The region in the square has been selected for EDX elemental analysis (Al/Si molar ratio of 3.44).

one micrometer and lengths of a few micrometers. Similar observations have also been made in many previous SEM pictures [5, 19, 25], despite the investigations made by different researchers and fly ashes taken from a variety of power plants.

Acicular forms have been previously regarded as the main characteristics of mullite, although irregular forms called chunky habit also occur in synthetic mullite [18]. In the SEM picture for ARFA in Figure 8, it is apparent that acicular crystals scatter in the disintegrated mass, with diameters of less than one micrometer and lengths of a few micrometers. Since size distributions have been measured by laser beams with the ARFA dispersed in water, the directions of acicular crystals may be at work, that is, the two peaks at $0.8\ \mu\text{m}$ and $2.3\ \mu\text{m}$ could actually reflect the average diameter and length of acicular crystals in disintegrated ARFA. In the selection region of SEM picture in Figure 8, an EDX analysis has been made to produce an Al/Si molar ratio of 3.44, which is in the neighborhood of 3 for ideal Al/Si molar ratio of mullite [18].

3.3. Dissolved Components and Glasses Compositions in Acid and Base Digestion Processes. Similar to the K_2O calculations in Section 3.2.1, the weight percentages of acid and base digestion ARFA in Figure 1 and the weight percentages of components in acid and base digestion ARFA in Figure 2 can be used to calculate the absolute weights of components in ARFA from acid and base digestion processes, and the dissolved components can be obtained by subtracting the components in acid and base digestion ARFA from those in the raw ARFA. In Figure 9, components are given in percentages of the total weight of dissolved components as a function of digestion time. Dissolved components come from glasses as well as other phases, and with the identification of glasses in ARFA in Section 3.2, the glass compositions can be obtained.

3.3.1. Dissolved Components and Glasses Compositions in Acid Digestion Process. In Figure 9(a) for dissolved components of ARFA in acid digestion process, from the beginning to the interval of 2 hr, the dissolved components tend to increase in SiO_2 and decrease in Al_2O_3 . According to Figure 7(a),

medium size particles of ARFA would be digested in the intervals up to 1 hr. According to Figure 5, ferrite spinel will be digested even in the interval of 15 min. According to Figure 9(a), CaO , TiO_2 , and Fe_2O_3 are also at the highest level in the beginning. These observations may mean ferrite spinel preferably occurs in medium size particles of ARFA, which could be partially composed of CaO and TiO_2 besides Fe_2O_3 [20, 21].

At the intervals of 2 hr and 4 hr in Figure 9(a), SiO_2 and Al_2O_3 reach the highest and lowest levels and tend to decrease and increase in the extended periods of acid digestion time. According to the K_2O standard with 7.1 hr as the time for complete glass digestion in ARFA, the glasses by acid digestion process would have the following compositions: SiO_2 62.8 wt%, Al_2O_3 22.9 wt%, CaO 5.1 wt%, TiO_2 2.9 wt%, Fe_2O_3 2.3 wt%, and K_2O 1.0 wt%. According to Figure 9(a), K_2O retains 1.0 ± 0.1 wt% till the interval of 8 hr, after which it slowly decreases to 0.8 wt% and 0.7 wt% with more components of ARFA being dissolved. Therefore, it can be said that “potassium appears to be reasonably well distributed throughout the glass” [19].

In Figure 9(a), it is also interesting to note that TiO_2 seem to be in parallel with Fe_2O_3 in a wide range, with TiO_2 slightly higher than Fe_2O_3 . This means the two components could have the same origin. Among the possible minerals with the approximate ratios of TiO_2 to Fe_2O_3 , ilmenite seems to be the most likely. However, in the XRD spectra for raw ARFA in Figure 4, no peaks could be clearly assigned to ilmenite. If ilmenite does occur in alumina rich coal (ARC), the combustion processes involving reduction and oxidation could have destroyed parts of the mineral for the formation of ferrite spinel [26–28].

3.3.2. Dissolved Components and Glasses Compositions in Base Digestion Process. In Figure 9(b) for dissolved components of ARFA in base digestion process, higher SiO_2 and lower Al_2O_3 are observed in step Base Dissolution I relative to the beginning of acid digestion process. There is also a higher K_2O of 2.0 wt% in this step due to the similarity dissolution principle. With step Acid Dissolution, hydroxysodalite covering ARFA is destroyed by HCl to release Al_2O_3 as AlCl_3 into solutions, and CaO , TiO_2 , and Fe_2O_3 are also readily dissolved. In step Base Dissolution II, as more SiO_2 is dissolved, other components decrease relatively in the dissolved components of ARFA. The glasses by base digestion method would have the following compositions: SiO_2 61.5 wt%, Al_2O_3 21.5 wt%, CaO 9.1 wt%, TiO_2 2.2 wt%, Fe_2O_3 2.2 wt%, and K_2O 1.1 wt%.

As discussed above, the glass compositions by base digestions are very similar to those by acid digestions, usually with 0.1–1.4 wt% difference for each component. One noticeable difference is a higher CaO in the glasses by base digestions, due to more CaO dissolved in step Acid Dissolution. The roles of additives on silicate glass structures can be very complicated, Na^+ , K^+ , Ca^{2+} , and Mg^{2+} are networking modifiers, and Al^{3+} can be either networking former or modifier [16, 29, 30]. Mixed layer smectite-illite clays have been reported to form a large proportion of minerals in the coals for power plants

FIGURE 9: Chemical composition changes of dissolved components of ARFA in acid digestion process (a) as a function of time and base digestion process (b) as a function of step.

[16]. In particular, illite is by definition potassic, and “fixed” potassium occurs completely in the interlayers. It has been generally agreed that K₂O or Na₂O would bridge SiO₂ and Al₂O₃ units in glasses. As more K₂O or Na₂O is added, more Al₂O₃ is taken up, and the glass content will increase in fly ashes [16, 29, 30]. According to Figures 3 and 9, over 95 wt% of K₂O distributes evenly in glasses. Therefore, it is suggested that illite could have been transformed into the glasses to incorporate potassium, which allows for some explanation of the K₂O standard.

3.3.3. Implications for Alumina Extraction from ARFA. According to the compositions and weights of glasses in Figures 1 and 9, for acid digestion process, there is 26.6 g SiO₂ in the digested glasses per 100 g ARFA, which should account for about 66.5 wt% of silica in ARFA. If the silica in glasses can be removed, then two thirds of CaO addition would be cancelled for alumina extraction from ARFA. However, with step Base Dissolution I in base digestion process, there is 13.8 g SiO₂ in the digested glasses per 100 g ARFA due to hydroxysodalite formation, which accounts for 34.5 wt% of silica in ARFA. Silica removal would be intensified in the predesilication process if hydroxysodalite formation can be checked. Such an idea has been partially realized in one recent paper, in which zeolite P was used to block the formation of hydroxysodalite, and a higher desilication rate has been achieved [12]. According to particle transformation in Figure 7(a) in acid digestion process, small particles are mostly disintegrated building pieces of ARFA, large particles would be etched in long time, and medium size particles are enriched in glasses and tend to be digested very rapidly. Therefore, if medium size particles could be screened out

prior to alumina extraction, the left ARFA would have less glasses and accordingly less SiO₂, resulting in a similar effect as predesilication.

4. Conclusions

The alumina rich fly ash (ARFA) with about 50 wt% alumina has been regarded as a real gift for China short of bauxite and brings about the hope for a self-contained alumina industry. For the many processes under development for alumina extraction from ARFA, silica should be reduced by predesilication to avoid the addition of enormous amounts of lime. Therefore, it is necessary to study the glasses in ARFA, which could be useful for the development and optimization of predesilication process.

In this work, chemical digestion methods were used to characterize the glasses in ARFA. The chemical compositions of acid and base digestion ARFA were measured by XRF. The K₂O standard was used for the process depiction of acid digestion and the estimation of glass amount in ARFA. The weight of glasses by acid digestion was 2.7% more than that by base digestion, and the formation of hydroxysodalite blocked the glass digestion. The FTIR and XRD spectroscopies provided the evidences for phase transformation, and the size analysis and SEM-EDX yielded rich information on particle transformations and identifications in acid and base digestion processes. Medium size particles were found to hold most of glasses in ARFA. The compositions for the digested components of ARFA in acid and base dissolutions were calculated, and the glass compositions were accordingly defined. The glass formation by illite could be the foundation for the K₂O standard for glass digestion in fly ashes. TiO₂ and

Fe_2O_3 in ARFA were found to be correlated and could have their origin from ilmenite. With these findings, this work has provided new knowledge on the glasses in fly ashes and suggested the ways to improve the pre-desilication process for alumina extraction from ARFA.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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