Original Paper

Liquid-Liquid Separation of Fine Zircon-Alumina Mixtures for Abrasives Recycling

Yoshihiro KANEMITSU*, Li Pang WANG, Gjergj DODBIBA
and Toyohisa FUJITA

Department of Systems Innovation, Graduate School of Engineering, The University of Tokyo,
Tokyo 113-8656, Japan

Abstract

A liquid-liquid separation method using aqueous and oil phases has been put forward for separation of fine zircon-alumina mixtures to recycle abrasives waste. By using a cation surfactant, zircon particles were made hydrophobic and extracted into the oil phase, whereas alumina remained in the aqueous phase. In this way, the fine zircon-alumina mixtures could be well separated. The result confirmed that the liquid-liquid separation method can be used to separate the fine zircon-alumina mixtures achieving relatively high grade and recovery.

Key words: Liquid-liquid separation, Alumina, Zircon, Abrasives, Iso-octane

1. Introduction

Japan is highly dependent on foreign countries for its metal supplies; therefore, it is essential that Japan use metal resources wisely and recycle them as much as possible. Almost all of Japan's metal resources are imported from foreign countries, and abrasives are in many cases made of valuable metals. Abrasives are very important to Japan's high-tech industry. The abrasives market in Japan has been gradually expanding. However, there has been little progress and research on recycling abrasives. Hence, recycling methods for abrasives shall be established to better use of Japan's important metal resources. This research was conducted to put forward a new method for recycling 400-ton-per-month abrasive wastes. The abrasives waste is generated from the manufacturing process. Abrasives with diameters $\pm 10 \mu\text{m}$ go to the market as products; the rest are sieved and dumped as waste, which amounts to about 400 tons per month¹. Generally speaking, abrasives product is a mixture of fine alumina and zircon¹. Thus, in order to recycle the waste, alumina and zircon need to be separated. Since alumina and zircon particles are very fine, a liquid-liquid separation

method was considered as the primary separation method. The liquid-liquid separation method uses two different solvents, a polar solvent and a non-polar solvent. During the liquid-liquid separation process, hydrophobic particles move to the non-polar solvent phase, and hydrophilic particles move to the polar solvent phase². Thus the separation is achieved. This method can separate particles of a few-micro-meter in diameter or less. A surfactant can improve the separation efficiency by changing the hydrophobicity of particles³.

2. Experimental

2.1 Sample and analysis methods

Reagents of α -alumina (Wako Co., Ltd., Japan) and zircon (Nacalai Co., Ltd., Japan) powders, with purity of 95 wt.% Al_2O_3 and 97.5 wt.% ZrSiO_4 , respectively, were used in this study. The zircon and alumina samples of special grade were mixed at a 1 to 1 ratio to provide the sample for this research. The zeta potentials of zircon and alumina were analyzed by a zeta potential analyzer (ZetaProbe, Agilent Technologies). The particle size distributions of zircon and alumina were analyzed by using a dynamic light-scattering apparatus (ELS-8000, Otsuka Electronics). Also, after the liquid-liquid separation process, the elemental compositions were analyzed by X-ray Fluores-

Accepted 23 April, 2012

*e-mail: tt116308@mail.ecc.u-tokyo.ac.jp

Fig. 1 Zeta potential of zircon and alumina as a function of pH

cence (XRF: Supermini, RIGAKU) to calculate the grades and recoveries.

2.2 Characteristics of sample

Figure 1 shows the zeta potential of zircon and alumina as a function of pH. Between pH 4 and 9, alumina and zircon are charged positively and negatively, respectively. With this characteristic, a cation surfactant was considered to be effective in making the negatively charged zircon particles hydrophobic and extract them into the oil phase, leaving alumina particles in the aqueous phase. The particle sizes of the alumina and zircon powders were $0.58 \pm 0.08 \mu\text{m}$ ($D_{50} = 0.59 \mu\text{m}$) and $0.6 \pm 0.19 \mu\text{m}$ ($D_{50} = 0.61 \mu\text{m}$), respectively.

2.3 Chemical reagents

Dodecylamine Acetate (DAA: $\text{C}_{12}\text{H}_{27}\text{N} \cdot \text{C}_2\text{H}_4\text{O}_2$) of the purity over 98% and iso-octane were used. HCl and NaOH were used to adjust the pH value of the aqueous phase.

2.4 Liquid-liquid extraction of zircon and alumina as preliminary experiment

In this preliminary experiment, zircon and alumina were separately tested to determine the pH value and DAA concentration at which zircon is extracted into the oil phase while alumina remains in the aqueous phase. 1.0 g of the zircon or alumina sample was dissolved and dispersed in 80 mL of ion-exchanged water by ultrasonic vibrations for 3 minutes. After the sample was suspended evenly in the aqueous phase, the pH of the mixture was adjusted with HCl and NaOH. Then, conditioning (shaking) was carried out for 15 minutes at the DAA concentration 0.0 or 0.48 kg/t. The unit measurement of kg/t is kilograms of DAA added per ton of zircon or alumina sample. After the conditioning, pH was readjusted by using HCl or NaCl. Then, 20 mL of iso-octane was added to the

mixture. The mixture was shaken for 15 minutes, and then it was allowed to settle for at least 10 minutes to form two separate phases. Then, the oil phase and aqueous phase were separated by centrifugal separation (KUBOTA 9000) at 3600 rpm for 30 minutes. After removing the supernatant liquid, the centrifugal tubes were dried in a drier at 90°C for more than a day. By comparing the original weights of the centrifugal tubes with their weights with the samples, the recoveries in the oil phase and aqueous phase were calculated. The calculated recoveries were then plotted as a function of pH.

2.5 Liquid-liquid separation of zircon-alumina mixture

1.0 g of the reagent zircon and 1.0 g of the reagent alumina were dissolved and dispersed in 80 mL of ion-exchanged water at an adjusted pH by ultrasonic vibrations for 3 minutes. After the mixed sample was suspended evenly in the aqueous phase, conditioning (shaking) was carried out for 15 minutes at a certain DAA concentration. After the conditioning, pH was readjusted with HCl and NaOH and measured by using HCl and NaCl. The unit measurement of kg/t is kilograms of DAA added per ton of the mixed sample. Then, 20 mL of Iso-octane was added to the mixture. The mixture was shaken for 15 minutes, and then it was allowed to settle for at least 10 minutes to form two separate phases. Then, the oil phase and aqueous phase were separated by centrifugal separation (KUBOTA 9000) at 3600 rpm for 30 minutes. After removing the supernatant liquid, the centrifugal tubes were dried in a drier at 90°C for more than a day. By comparing the original weights of the centrifugal tubes with their weights with the samples, the recoveries in the oil phase and aqueous phase were calculated. Then, the particles extracted to the oil and aqueous phases were analyzed for zircon and alumina by using XRF. Grades were calculated by using the standard curve prepared in advance. The calculated recoveries and grades were then plotted as a function of the DAA concentration or pH.

3. Results and Discussions

3.1 Results of liquid-liquid extraction of zircon and alumina

Figures 2 and 3 show the experimental results which suggested that 97% of zircon was recovered in the oil phase at pH 3.5 at the DAA concentration of 0.48 kg/t (see Figure 4). The results demonstrated that pH played an important role in recoveries of zircon and alumina in the oil phase.

Fig. 2 Recovery of zircon in the oil phase as a function of pH

Fig. 3 Recovery of alumina in the oil phase as a function of pH

Also, a high recovery of zircon was obtained at pH 6.5 at the DAA concentration 0.48 kg/t. The two peaks observed in the zircon recovery curve is explained as follows:

- (1) The first peak at pH 3.5 is because of the low electric charge on the zircon surface. Since the low electric charge on the surface means that zircon particles coagulate easily, at pH 3.5 the zircon was extracted into the oil phase with the highest recovery of 97%.
- (2) The second peak at pH 6.5 is due to the high negative charge on the zircon surface. Although zircon is rather hydrophilic in this state, DAA's cation is easily adsorbed to the negatively charged zircon, making the zircon highly hydrophobic. Since zircon's zeta potential is low (high negative charge) at pH 6.5, DAA is easily adsorbed to zircon at this pH value. Thus, this condition yielded the second highest recovery of 95%.

As for alumina, 99% recovery was obtained at pH 7.4 and 8.2. Alumina is charged positively at a wide range of pH values. However, the positive charge starts to decline around pH 7. The decline in the positive charge allows DAA molecules, which have positive charges, to be adsorbed to alumina. Therefore, the highest recovery was observed at pH 7.5 and 8.3. At pH values higher than

Fig. 4 Zircon extraction at pH 3.5

9, DAA becomes ineffective, because the chemical equilibrium of DAA is possible in the presence of abundant protons. This explains the low recovery of alumina at pH 9 in spite of the fact that alumina is no longer charged positively at this pH.

At pH 3.5, almost all the alumina remained in the aqueous phase, while 97% zircon was extracted into the oil phase. This suggested that at pH 3.5 the zircon-alumina mixture could be separated by using the liquid-liquid separation method.

3.2 Results of liquid-liquid separation of zircon-alumina mixture

Results are shown in Figure 5 and 6. Figure 5 suggested that the DAA concentration can be optimized at a fixed pH value. Figure 6, on the other hand, showed pH played an important role in determining recoveries and grades at a fixed DAA concentration. The highest grade of zircon in the oil phase was 79.2%, with a recovery of 56.7% at pH 3.90 and DAA 1.92 kg/t. The highest grade of alumina was 100% at pH 7.00 with a 6.5% recovery. At pH 3.5, which was optimum in the liquid-liquid extraction experiment, the separation was not very effective. Better results were obtained around pH 4. Around pH 7, most of the zircon-alumina mixtures were extracted into the oil phase, leaving little high-grade alumina in the aqueous phase.

Since the objective of this research was the separation of zircon-alumina mixtures, obtaining a high grade was more important than a high recovery.

Fig. 5 Zircon recovery and grade in oil phase and alumina recovery and grade in aqueous phase at pH 3.9 as a function of the DAA concentration

Fig. 6 Zircon recovery and grade in oil phase and alumina recovery and grade in aqueous phase at DAA 0.96 kg/t as a function of pH

ery. Also, considering the fact that zircon is about twice more expensive than alumina, zircon grade was set as the priority. The highest zircon grade in the oil phase, 79.2%, and recovery, 56.7%, at pH 3.90 and DAA 1.92 kg/t are considered satisfactory. In this condition, the alumina grade and recovery in the aqueous phase were 59.4% and 81.0%, respectively. However, the pH 3.90 was not the expected optimum pH 3.50 as seen in the preliminary liquid-liquid extraction experiment. When zircon was processed separately, the highest recovery in the oil phase was obtained at pH 3.50. At this pH, at the same time, most of the alumina remained in the aqueous phase. Thus, it was assumed that pH 3.5 would provide the best condition. At pH 3.50 most of the zircon-alumina mixture remained in the aqueous phase, with the weight ratio between the oil and aqueous phase extracts 20 to 80. This result was contrary to that of the preliminary experiment, where zircon was extracted into the oil phase at pH 3.5 with the recovery 97%. This is explained by using a model shown in Figure 7. At pH 3.5, the zeta potential of zircon is near zero. Since a low zeta potential means that particles are likely to coagulate, zircon in a solution of pH 3.5 was expected to coagulate. At pH 3.5, alumina's zeta potential is very high and above 30 mV. This suggests that alumina particles

Fig. 7 Coagulation model of the phenomenon at pH 3.5

were suspended evenly without coagulating with one another, repelling each other. Thus, while mixed together, alumina and zircon particles can form such a cluster as illustrated in Figure 8. In this model, coagulated zircon particles were surrounded by bigger alumina particles, and the alumina particles repel DAA molecules with their positive charges. This explains the reason why most of the mixture remained in the aqueous phase.

4. Conclusions

- (1) When the liquid-liquid extraction was applied to zircon, the recovery was highest (97%) at pH 3.5 and DAA 0.48 kg/t.
- (2) After applying the liquid-liquid separation to fine zircon-alumina mixtures, the highest zircon grade in the oil phase, 79.2%, and recovery, 56.7%, were obtained at pH 3.9 and DAA 1.9 kg/t.
- (3) The highest grade of alumina obtained was 100% at pH 7.00 and at DAA 0.96 kg/t with a 6.5% recovery.

Acknowledgement

The authors were supported by the the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (A) (22246118).

References

1. Private Communication, Fujimi Incorporated, June 2011.
2. A. Otsuki, G. Dodobiba, A. Shibayama, J. Sadaki, G. Mei, T. Fujita: *J. Applied Physics*, **47**, No. 6, pp. 5093–5099 (2008)
3. B. Hu, E. Kuzuno, T. Fujita, M. Mamiya: *J. MMIJ*, **109**, pp. 367–372 (1993)