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Removal of oil from ferrous grinding swarf of automobile industry by aqueous washing process

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ABSTRACT

This research focused on the recovery of valuable materials from ferrous grinding swarf. We received the sample from the automobile industry. The sample has consisted of approximately 20 wt% moisture and 80 wt% residue (oil and soild). The chemical composition of the oven-dried sample was approximately 87 wt% iron. In this study, aqueous washing process for oil removal from ferrous grinding swarf was investigated with two different commercial reagents, Micro-90 and Detergent 8. Three different amounts of solids (2, 3, and 4 g) were mixed with 20 mL of diluted reagents for the aqueous washing. In the Micro-90 solution, about 80% of the oil was removed after three washing cycles at a solids content less than 3 g/20 mL. On the other hand, when using Detergent 8, 100% oil was removed after three washing cycles at a solids content of less than 3 g/20 mL. Pulp density was an important factor in determining oil removal efficiency. For the scale-up experiment, different washing methods such as ultrasonication and overhead stirrer were examined. The preliminary reuse test of the Detergent 8 solution was also conducted for the feasibility of the aqueous washing process.

1. Introduction

The automotive industry has made enormous progress in terms of production and technology over the last decade. Although researches on light materials, such as aluminum, has recently been carried out to reduce the weight of automobiles, iron is still the most important material for automobile parts. Ferrous grinding swarf is produced during the machining process including turnings, filings, and shavings in automobile and aerospace industries. It is a mixture of small metal particles, metal removal fluid, lubricants, moistures and oil residuals from grinding media (Ruffino and Zanetti, 2008; Chang et al., 2006; Fua et al., 1998). The exact amount of ferrous grinding swarf generated in the world is unknown due to the lack of statistical information. The technical paper reported that more than 40,000 tons of swarf is generated every year by only one of the three major auto producers (Hess and Kawatra, 1999).

Metalworking fluids provide better-grinding properties by lubricating and cooling the interface between tool and material, and prevent thermal damage (Irani et al., 2005). However, oil residue covers metal grindings and ceramic particles after its work, therefore it can difficult recovery of metals using the leaching process. Oil, also found in grinding swarf, causes technical problems in remelting processes. Oil residuals may explosively burn or generate undesirable pollutant compounds in burning emissions (Ruffino and Zanetti, 2008). Recently, as environmental regulations related to environmental pollution have been strengthened, eco-friendly technologies to reduce environmental pollution and to recover resources are being studied (Lee et al., 2017). Especially in the machining and machinery industries, interest in how to handle the recycling of metal swarf and cutting fluids management (Lee et al., 2017; Salihoğlu and Çelikli, 2018).

In terms of removal of oil and recovery of resources, some researchers have conducted cleaning studies of oil-containing grinding swarf using commercial surfactants (Chang et al., 2006; Fua et al., 1998; Fua and Matthews, 1999; CWC, 2000). Ruffino and Zanetti (2008) carried out the cleaning process using various surfactants such as sodium dodecylbenzene sulfonate salt (SDS), docusate sodium salt ($C_{20}H_{37}NaO_7S$), N-lauroylsarcosine sodium salt ($C_{15}H_{28}NNaO_3$) sodium cholate hydrate ($C_{24}H_{39}NaO_5 + H_2O$) and choline chloride ($C_5H_{14}ClNO$). They also evaluated cost analysis for the economic advantage of the treatment (Ruffino and Zanetti, 2008). Fua et al., 1998 and CWC (2000) performed

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bench-scale studies of aqueous surfactant washing and they found that a strong dependence of the aqueous washing efficiency on the choice of a suitable surfactant. Jean et al. (1999) studied the separation of oil from oily sludge by freezing and thawing. Aqueous washing process using commercial surfactants has also been applied to clean the contaminated soils (Deshpande et al., 1999). If an aqueous process implemented successfully, for the separation of metal and oil from raw swarf, metallic fines could be reused by the metal industry and the oil would be recycled as cutting oil or fuel (Chang et al., 2006). Swarf would then become an asset containing iron powder rather than a waste for manufacturers (Takagi et al., 2011).

The ferrous grinding swarf is an inevitable by-product of the automotive processing industry, as well as that of the steel product manufacturers using subtractive manufacturing. In our study, one of the leading automotive manufacturers in North America generated about 27,500 net tons of ferrous swarf (on a wet basis) in one location alone. Nevertheless, the technique of recovery of metals and the treatment of oil will increase the value of metals and reduce process costs. In this study, we investigated oil removal from ferrous grinding swarf using commercial detergents, such as Micro-90 and Detergent 8, that have not been applied so far. In addition, we compared the oil removal efficiency, by changing the solid–liquid ratio and washing methods, to find the optimal oil removal conditions and also conducted preliminary tests to reuse the detergent solutions.

2. Experimental

2.1. Materials

The ferrous grinding swarf was obtained from the automobile industry in North America. Fig. 1(a) shows the image of the as-received ferrous grinding swarf. The relatively wide size distribution of the sample can be observed in the photo. It was agglomerated together to form a large size due to its moisture and oil residue. Fig. 1(b) shows the SEM image with EDS results. As shown in Fig. 1(b), the sample comprises metal grindings and ceramic particles, and the size of ceramic particles is about 100 μm. Ceramic particles mostly can come from the grinding wheel since it can be broken during its grinding operation. Metal grinding was approximately 87 wt% iron.

2.2. Characterization of the ferrous grinding swarf

2.2.1. Physical properties of the ferrous grinding swarf

In this study, an analysis of moisture and oil content is the most important to determine the physical properties. Based on these results, we can suggest appropriate iron recovery methods. The moisture content of as-received ferrous grinding swarf was determined using on the ASTM standard method D2216-10. 20 g of the pretreated sample was placed in a porcelain crucible and this sample was dried at 110 °C. The percentage of moisture in the sample is calculated based on the following equation:

$$m = \frac{M_{cms} - M_{cds}}{M_{cds} - M_c} \times 100 = \frac{M_m}{M_s} \times 100 \quad (1)$$

m = moisture content, %
M_{cms} = mass of container and moisture specimen, g
M_{cds} = mass of container and oven dry specimen, g
M_c = mass of container, g
M_m = mass of moisture $(M_m = M_{cms} - M_{cds})$, g
M_s = mass of oven dry specimen $(M_s = M_{cds} - M_c)$, g

Based on the Eq. (1), the moisture content of the samples was about 20 wt% and not changed by time after 2 h of drying.

It is important to know the amount of oil residue in the ferrous grinding swarf. There were some methods for oil analysis including Total Organic Carbon (TOC), Total Recoverable Petroleum Hydrocarbon (TRPH), and a gravimetric method (Fua et al., 1998). Urum et al. (2006) also investigated the distribution of hydrocarbons on contaminated soils including crude oil by Gas Chromatography Mass Spectrometry (GC/MS) analysis. In this study, the oil content of the sample was determined by the gravimetric method with aqueous washing process (Ruffino and Zanetti, 2008). This method consists of acetone washing and water rinsing. For the analyses, 2 g of oven-dried sample was mixed with 20 mL of acetone, and the oil in the sample was washed for 30 min by ultrasonic cleaning. The liquid fraction was then decanted and the precipitated solid was rinsed with 60 mL of water for 10 min by ultrasonication. The above procedures were repeated twice and the solution was decanted. After aqueous washing steps, the sample was dried in a drying oven at 110 °C for 3 h. The final weight of the sample was compared to the initial mass to obtain the oil content of the ferrous grinding swarf. Experiments were conducted three times to measure the consistency in oil content since oil contamination could have a deviation from each other. The percentage of oil removal increases with washing cycles and it reaches a constant value at about 16 wt%. Based on the results, we considered the sample had approximately 16 wt% of oil residue.

2.2.2. Chemical properties of the ferrous grinding swarf

Chemical composition of as-received ferrous grinding swarf was measured with the inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (Optima 8000, Perkin Elmer). 0.1 g of oven dried sample was mixed with 1 g of flux (60% lithium metaborate ($LiBO_2$) and 40% lithium tetraborate ($Li_2B_4O_7$)) in a graphite crucible. After that, the sample was fused in a muffle furnace at 1100 °C for 1 h. The molten samples were digested in a 25 vol% of nitric acid (HNO_3, 68–70%, GR ACS), and diluted with 2 vol% of HNO_3 before the ICP-OES analyses. Table 1 shows the chemical compositions of the sample. Based on the results, iron content in the sample was 86.5 wt%, and the sample also contained a small amount of copper, manganese, aluminum, and other elements.

The particle size of the ferrous grinding swarf was analyzed with a laser particle size analyzer (Malvern Mastersizer 3000). As shown in Fig. 1(c) shows the cumulative particle size distribution of the ferrous grinding swarf. D-values, which can be considered as the diameter of the samples, often used when describing particle size distributions. D-values (D10, 50, and 90) intercepts for 10%, 50% and 90% of the cumulative volume. Based on Fig. 1(c), these values were 18.4, 77.0, and 513 μm, respectively. In addition, the phases crystalline of the sample were analyzed by the X-ray diffraction (XRD, Empyrean, PANalytical). For the XRD powder analyses, the ferrous grinding swarf was dried to remove water and it was ground to break the agglomerated powders. Cr target was used, instead of Cu target, to minimize the fluorescence problem of the iron during the XRD analysis. As shown in Fig. 1(d), Fe and $Fe_{1.9}Si_{0.1}$ was the main chemical phases of the sample. For the quantitative phase analysis, a Rietveld refinement technique was applied to the data by the X'pert HighScore Plus software. The sample contains about 30% of Fe and 70% of $Fe_{1.9}Si_{0.1}$. This result indicated that metallic iron was the main component of the sample rather than iron oxides. Also, the sample contains a small amount of silicon due to the grinding media.

2.3. Oil removal from ferrous grinding swarf by aqueous washing

Oil residue in the sample can affect the feasibility of metal recovery since it burns explosively during the smelting operation.

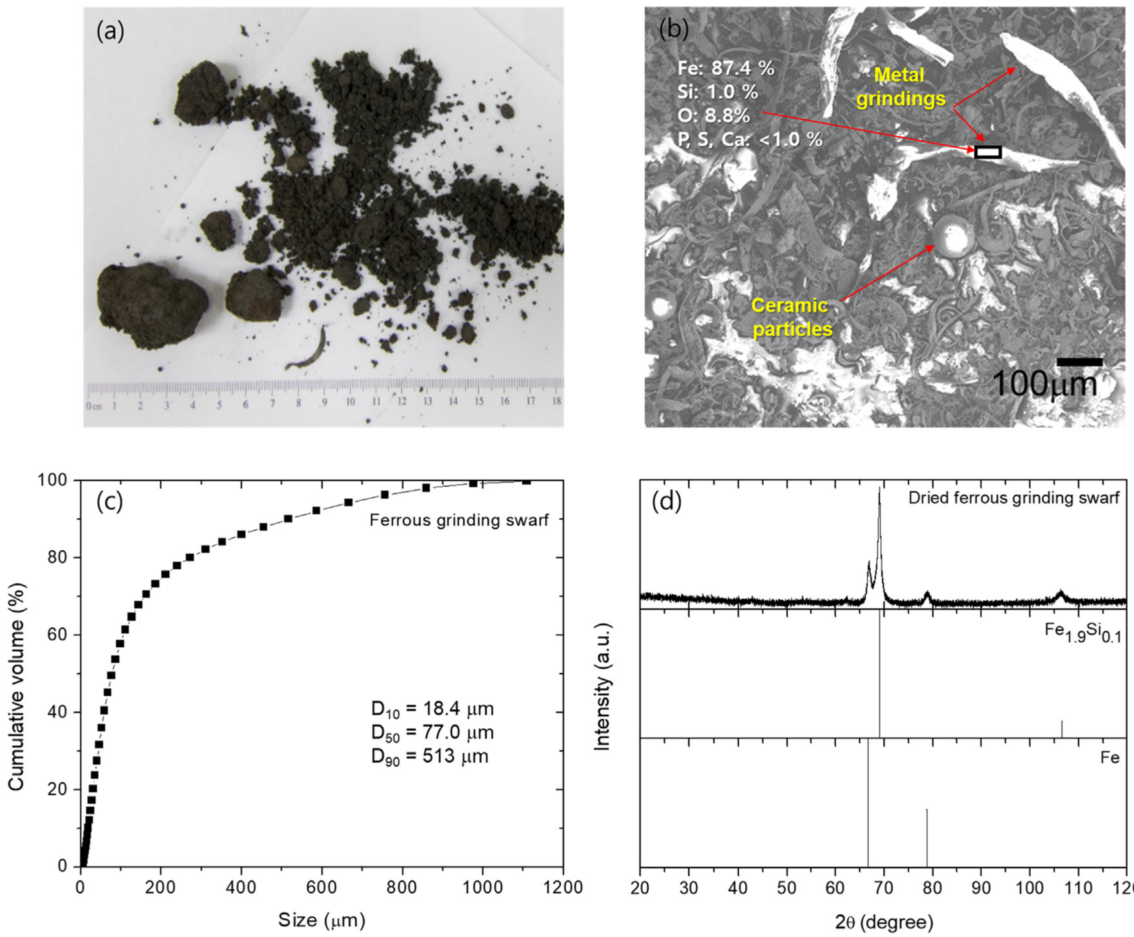

Fig. 1. Sample information: (a) ferrous grinding swarf; (b) SEM image; (c) size distribution and (d) XRD pattern.

Table 1
Chemical composition of the oven dried ferrous grinding swarf by ICP-OES.

Element	Si	Ni	Fe	Mn	Al	Ca	Mg
Wt.%	1.3	0.1	86.5	0.5	0.8	0.3	0.2

For this reason, we first tried the aqueous washing process to remove oil in the ferrous grinding swarf. Two different reagents, detergent-8 (Alconox, Inc.) and Micro-90 (International Products Corp.), which is a commercial cleaning solution, were used to remove oil residue at different washing conditions. Experimental procedures for aqueous washing are shown in Fig. 2. It represents one cycle of our aqueous washing process. (1) The oven-dried sample was mixed with 20 mL of reagents, and (2) the oil residue in the sample was washed for 30 min within the ultrasonic bath. (3) The liquid fraction was then decanted and (4–5) the precipitated solid was rinsed with 60 mL of water for 10 min by ultrasonication. (6) The water was then decanted. After aqueous washing steps, the oil-removed sample was dried in a drying oven at 110 °C for 3 h. Three repeat experiments were carried out for a test condition in order to minimize the sampling error. The final weight of the sample was compared to the initial mass to obtain the oil content after the aqueous washing process. The oil removal efficiency was determined by comparing the value with the oil content (16 wt%) of the initial oven-dried sample. In addition, the chemical composition of ferrous swarf after aqueous washing process was analyzed by X-ray fluorescence (XRF, Olympus Corp.).

3. Results and discussion

3.1. Effect of reagents and solid contents on oil removal

Aqueous washing process of oil residue was conducted with two different reagents, Micro-90 and Detergent 8. Micro-90 is a chelating detergent, which contains EDTA salt, ionic and non-ionic ingredients. On the other hand, Detergent 8 is an ion-free detergent, which contains alkanol amine, glycol ethers, and alkoxylate fatty alcohol. Both reagents were diluted to 2% with DI water before cleaning applications. Three different amounts of solids (2, 3, and 4 g) were mixed with 20 mL of diluted reagents for the aqueous washing.

The percentage of oil removal of ferrous swarf after aqueous washing with the Micro-90 is shown in Fig. 3. As shown in Fig. 3 (a), about 80% of the oil was removed after three washing cycles at a solids content less than 3 g/20 mL. When the solids content was 4 g/20 mL, the efficiency of oil removal was significantly decreased from 80% to 20%. The efficiency of aqueous surfactant washing is primarily determined by the surfactant's ability to disperse, transport, solubilize and thus remove the contaminant

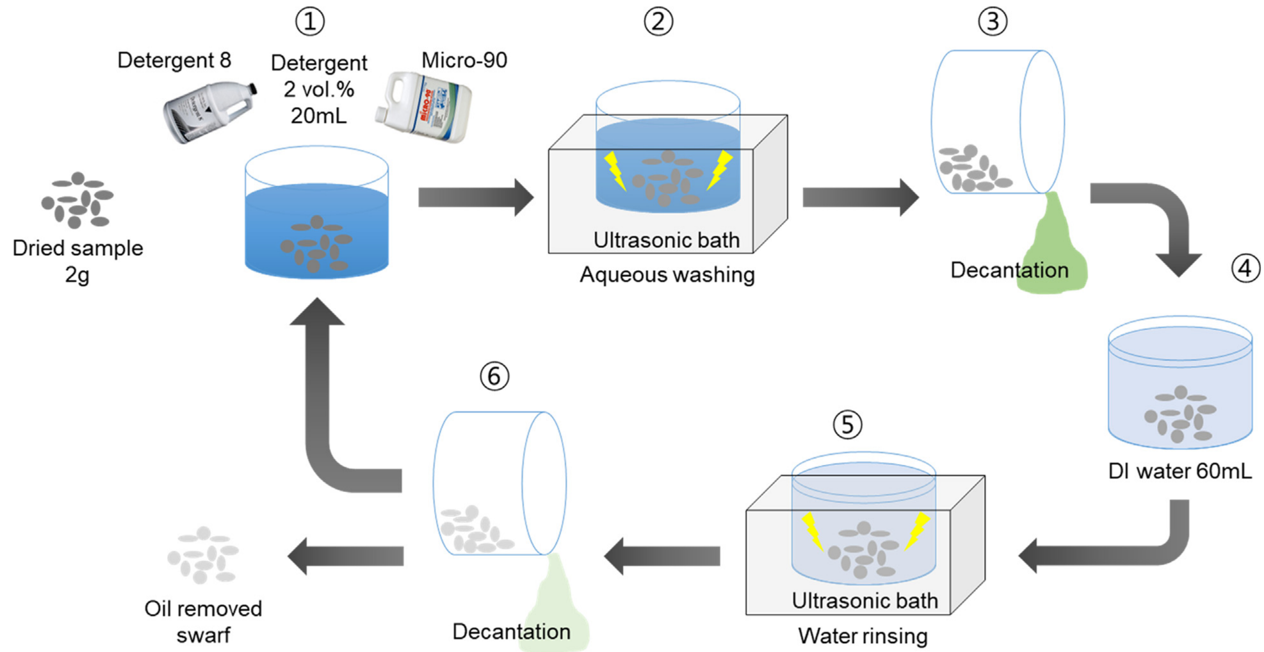

Fig. 2. Experimental procedures of oil removal tests.

molecules from the solid matrix (Fua et al., 1998). It is considered that the reason for the oil removal efficiency to decrease as the pulp density increases is that the sample particles are more agglomerated as the pulp density increases so that the contact between the particles and the surfactant is difficult. This means that the pulp density played a significant role in removing oil from

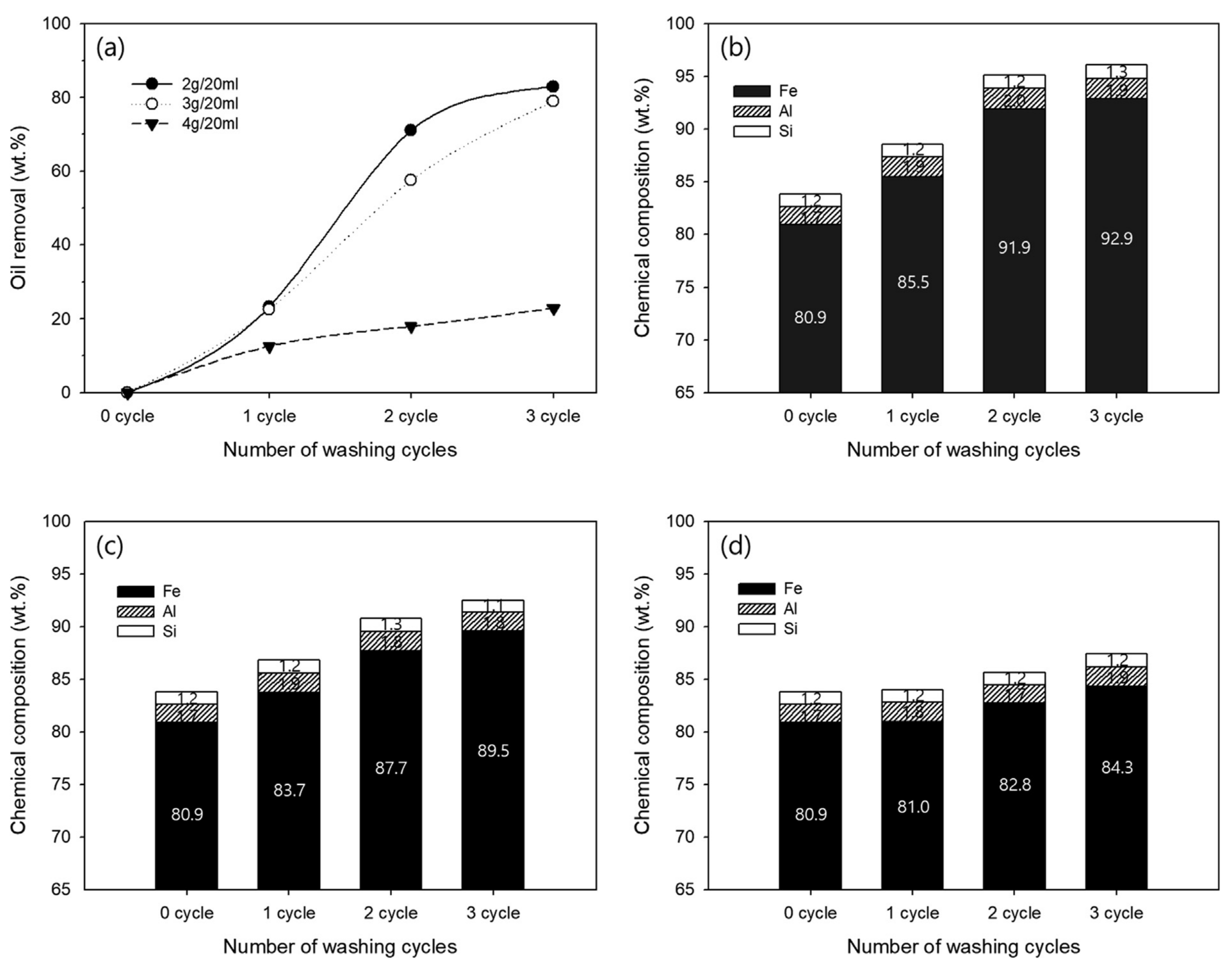

Fig. 3. Aqueous washing process with 2% Micro-90: (a) percentage of oil removal, and chemical composition with pulp density (b) 2 g/20 mL; (c) 3 g/20 mL; (d) 4 g/20 mL.

grinding swarf. Li et al. (2012) investigated the solvent extraction for heavy crude oil removal from contaminated soils and the oil removal efficiency has also changed with the change in solvent soil ratio (v/w). As shown in Fig. 3(b, c and d), iron content of the ferrous grinding swarf was concentrated from 80.9% to 92.9% after three washing cycles at a solids content of 2 g/20 mL (Fig. (b)). On the other hand, as the solid content increased, the rate of increase of iron composition decreased. As a result, the final composition of iron was 92.9%, 89.5% and 84.3% at 2, 3, and 4 g (with 20 mL), respectively.

When using Detergent 8 (Fig. 4), almost oil was removed after three washing cycles at a solids content of less than 3 g/20 mL. However, when the pulp density was increased, the oil removal efficiency was decreased from about 100% to 70% (Fig. 4(a)). As shown in Fig. 4(b and c), iron content of the ferrous grinding swarf was concentrated from 80.9% to 94.4 and 94.7%, respectively. On the other hand, at a solids content of 4 g/20 mL (Fig. 4(d)), the rate of increase of iron composition decreased. As a result, the final composition of iron was 94.4%, 94.7% and 87.5% at 2, 3, and 4 g (with 20 mL), respectively. Compared to the aqueous washing with Micro-90, Detergent 8 shows a better oil removal efficiency as shown in Figs. 3(a) and 4(a). Iron content was increased up to 94.7% after aqueous washing with Detergent 8 at a solids content less than 3 g/20 mL.

Fig. 5 shows the correlation between the oil removal rate and iron composition change. As shown in Fig. 5, the slope was close to linear, with the R^2 value of 0.9282. That is, as the oil was removed from the ferrous grinding swarf, the composition of the iron was increased constantly.

Based on previous results, Detergent 8 was selected as a reagent for the following two aqueous washing tests: (1) effect of sonication time and washing method on oil removal, (2) solution reuse after oil removal.

3.2. Effect of sonication time and washing methods on oil removal

Sonication time can affect the overall throughput, as well as operating cost, since ultrasonication requires electricity. For this reason, we changed sonication time, from 30 min per cycle to 10 min per cycle, to increase the process throughput and decrease the operating cost. 4 g of oven-dried ferrous grinding swarf was mixed with 20 mL of 2% Detergent 8 for the test. After first washing cycle, the percentage of oil removal was similar; however, it decreased from 68% to 55% after three washing cycles, as shown in Fig. 6(a). From this result, a longer sonication time showed a better oil removal, allowing more chance to detach adsorbed oil residue from the metal surface.

For the scale-up experiment, different washing method such as ultrasonication and overhead stirrer were examined, as shown in Fig. 6(b). To compare the oil removal efficiency between ultrasonication and overhead stirrer, 10 g of the sample was mixed with 100 mL of the solution and the oil residue was washed three times. Based on Fig. 6(b), aqueous washing with ultrasonication method shows a higher iron content compared to that of an overhead stir-

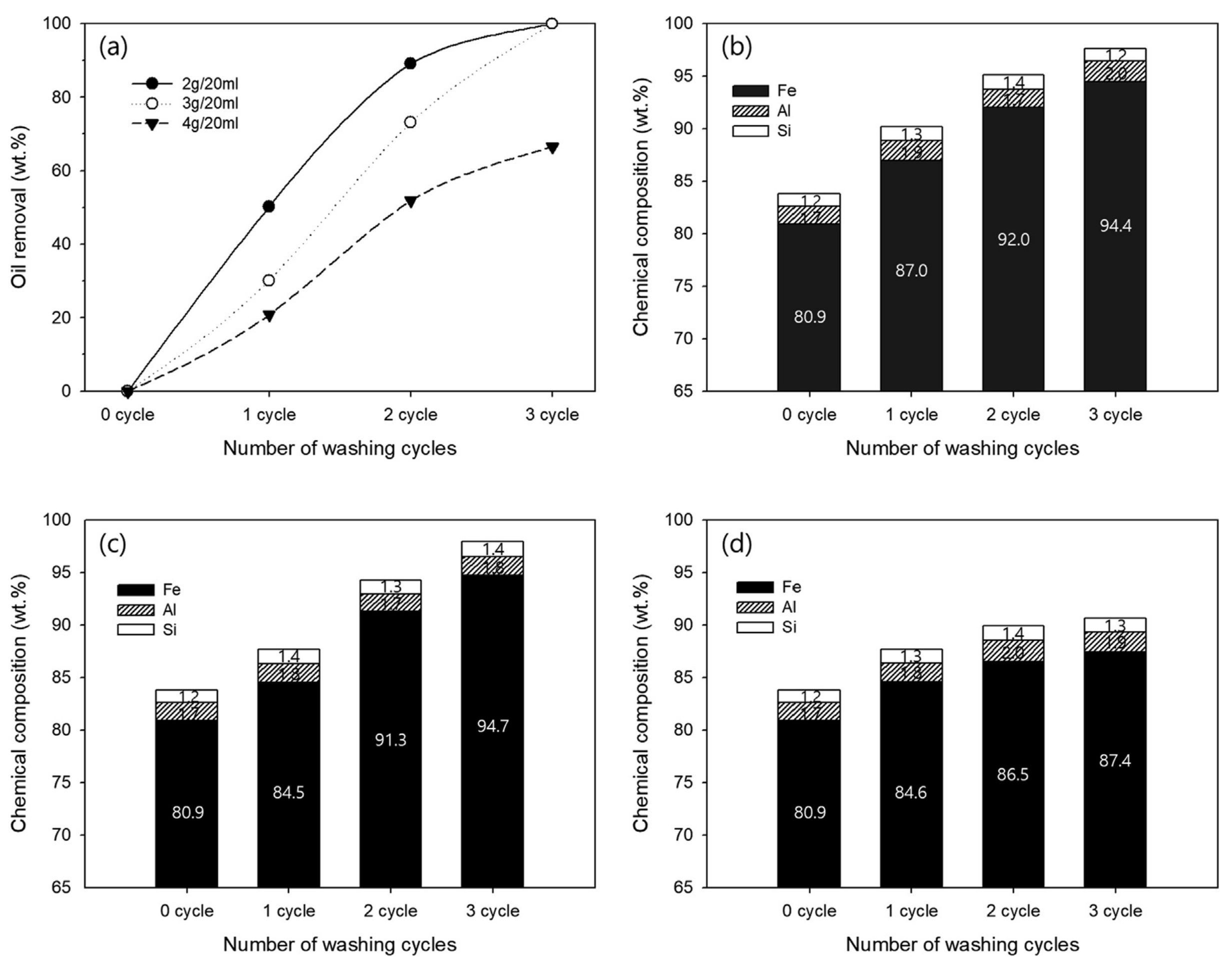

Fig. 4. Aqueous washing process with 2% Detergent 8: (a) percentage of oil removal, and chemical composition with pulp density (b) 2 g/20 mL; (c) 3 g/20 mL; (d) 4 g/20 mL.

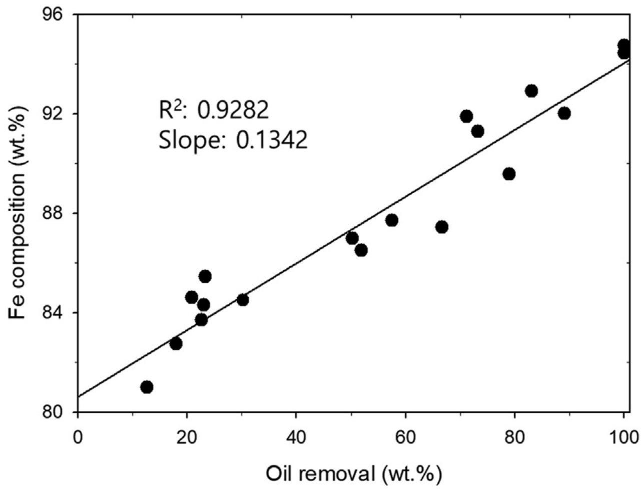

Fig. 5. The correlation between the oil removal rate and iron composition.

rer. The composition of iron was 87.2% and 84.2% at ultrasonication and overhead stirrer method, respectively. Based on the results, there was no significant difference in the composition of iron between the two processes. Therefore, an overall economic analysis, including the operating costs of both processes for the scale-up, is needed.

3.3. Preliminary tests for solution reuse after oil removal

Feasibility of solution recovery, after aqueous washing, is essential to the process of economics since we focused on the recovery of metallic iron after oil removal. Iron is a low-value item for metal recovery compared to other metals; therefore, reuse of the Detergent 8 solution, after aqueous washing step, was conducted in this research. A schematic diagram of the solution reuse is shown in Fig. 7(a). A total of three ultrasonic cleaning processes were carried out in this study, and three clean detergents were used. According to the experimental results shown in Fig. 4(b), the iron content greatly increased from 80.9% to 87.0% after the first washing cycle.

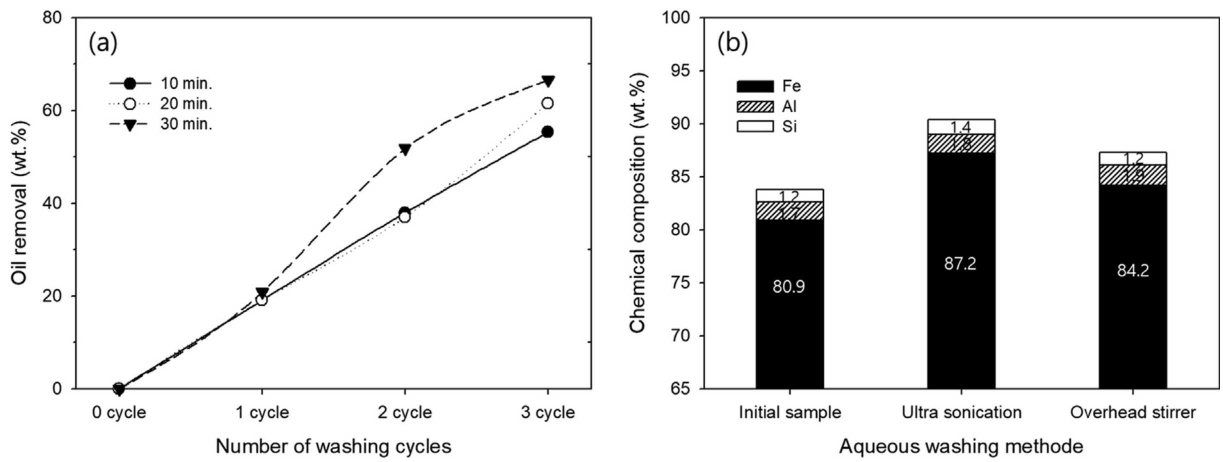

Fig. 6. Effect of oil removal with (a) sonication time; (b) washing methods.

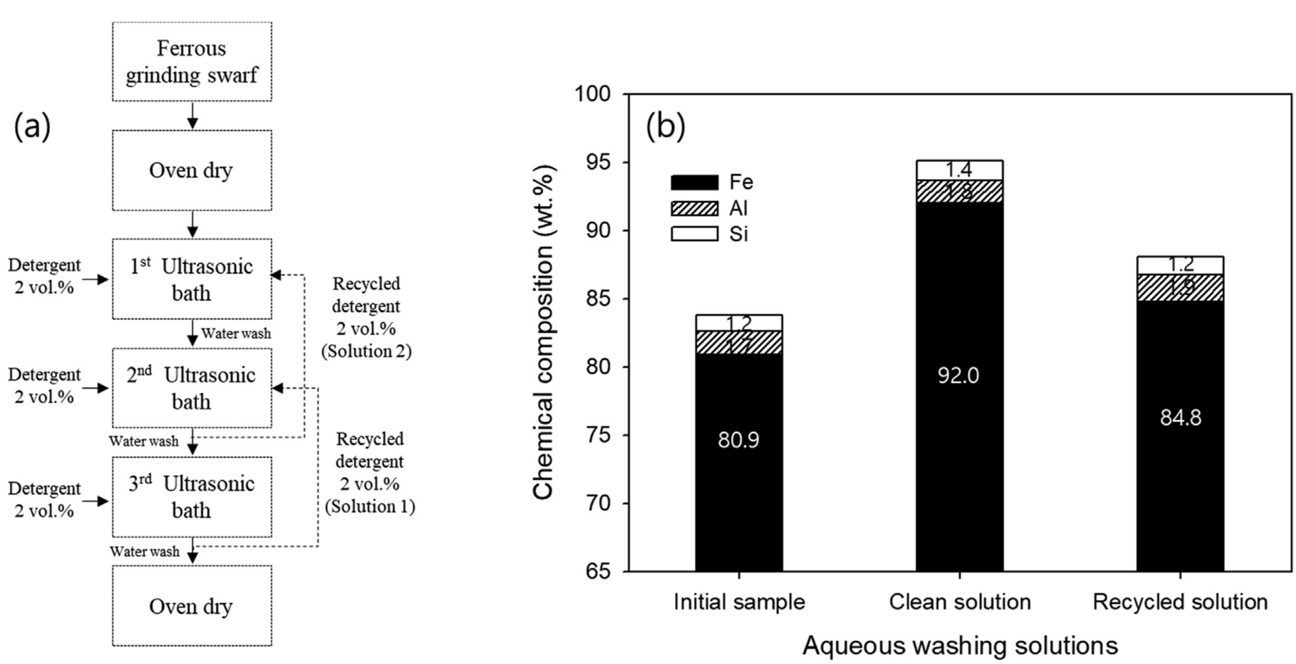

Fig. 7. Solution reuse system (a) schematic diagram; (b) chemical composition of ferrous swarf after clean and recycled solution washing.

On the other hand, after the third washing cycle, the iron content slightly increased from 92.0% to 94.4%. That is, after the third washing step, the solution (solution 1) can be reused since it is a less contaminated solution. Therefore we reused solution 1 as a second washing process solution. In the same way, solution 2 was reused to clean the oven-dried swarf in the beginning. With this experimental procedure, the amount of solution, what we used for the sample cleaning, was decreased by one-third.

Fig. 7(b) shows the oil removal rate and iron composition of clean detergent solutions and reused detergent solutions after the second washing process. Although the composition of iron was reduced from 92.0% to 84.8% when the solution was reused, we were able to confirm the possibility of removing oil by only conventional detergents. Further economic analysis of the aqueous washing process is required, and other processes such as the thermal process will be carried out for comparing the possibility.

4. Conclusion

For the recovery of ferrous grinding swarf, we focused on the oil removal by aqueous washing to recover metallic iron. From the preliminary oil removal experiment, Detergent 8 showed a better oil removal efficiency than Micro-90. At a less than 3 g/20 mL, Detergent 8 removed 100% oil residue from the ferrous grinding swarf after three washing cycles and iron content was increased from 80.9 to 94.7 wt%. This means that the pulp density played a significant role in removing oil from swarf. We also investigated the correlation between the oil removal rate and iron composition change. As a result, as the oil was removed from the ferrous grinding swarf, the composition of the iron was increased constantly. Aqueous washing process continuously requires surfactants, and wastewater containing oil is generated, therefore, further research is needed, such as the reuse of detergent solutions and recovery of oil, for a feasible ferrous grinding swarf recycling process.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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