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SEPARATION PROCESSES FOR RECOVERING ALLOY STEELS FROM GRINDING SLUDGE: SUPERCRITICAL CARBON DIOXIDE EXTRACTION AND AQUEOUS CLEANING

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ABSTRACT

Two separation processes have been developed to remove contaminants (cutting oil with trace phosphorus additive) from high-speed steel grinding sludge. One process uses an aqueous surfactant washing technique, and the second process uses supercritical carbon dioxide ($SCCO_2$) extraction. Our bench-scale aqueous washings have shown that the required phosphorus removal is easily obtained, but a sufficient oil removal is more difficult. The experimental results also indicate a strong dependence of the aqueous washing efficiency on the choice of a suitable surfactant. A mass transfer model is used to simulate a semi-continuous washing process. $SCCO_2$ extraction at 80 ^{0}C and 340 atm shows that approximately 80% of the oil can be removed from the sludge during a 60-minute process to produce a batch of recyclable steel, and that the phosphorus removal also reaches the required level. A linear desorption model is used to describe the irreversible desorption of oil from the solid phase into the CO_2 phase, and the simulated results agree very well with the experimental data.

INTRODUCTION

The manufacture of high-speed steel (HSS) cutting tools produces a large stream of oily solid waste, called grinding sludge, which comprises microscopic steel grindings, grinding media (non-metallic particulates such as silicon carbide, aluminum oxide, etc.),

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and other non-hazardous solids, all of which are covered with a residue of adsorbed cutting oil. This oil is used as a grinding lubricant and usually contains a phosphorus ester, a water-soluble additive that is introduced to improve the tribology of the grinding process. Presently, this solid waste is disposed in landfills. However, landfilling incurs a significant disposal cost as well as potential environmental liabilities and will be challenged by the increasingly strict environmental regulations. In addition, this operation causes a serious loss of high-quality alloy steel (15 million pounds per year in the US, equivalent to almost 40% of the raw materials). An alternative to this environmentally and economically unsound practice is to implement a cleaning and recycling process for this solid waste. Substantial research has been conducted to develop a successful procedure to separate and recycle the HSS and cutting oil from grinding sludge, so the alloy steel fines can be remelted by the HSS suppliers, and the lubricating oil can be reused by the cutting tool industry.

A complete recovery and recycling procedure for this waste involves several steps, such as cutting oil and phosphorus additive removal, metallic/non-metallic separation, and downstream treatment, but removing oil and phosphorus from the solid matrix is the first and most important step and is the focus of our research. The technical criteria for the acceptable recycled product require that it contain 0.03% or less by weight of phosphorus and must be low in oil content (approximately <5 wt%).

TWO SEPARATION PROCESSES

Two separation processes, using different cleaning approaches, have been evaluated for cutting oil and phosphorus additive removal: (1) aqueous surfactant washing, and (2) supercritical carbon dioxide ($SCCO_2$) extraction. Although they are both applicable to cleaning grinding sludge, these two methods have different process requirements and cleaning mechanisms. Aqueous washing is a low-pressure process involving the use of expensive specialty surfactant packages, and recovery of water and surfactant is an important consideration that will affect the economic situation of the project and thus the practicality of this procedure. $SCCO_2$ extraction is not as familiar a technology. It utilizes the increased solvating power of CO_2 at the temperatures and pressures above its critical point ($T_c = 31.1\ ^0C$, $P_c = 78.0$ atm). The most notable attractive features of this technique are that CO_2 leaves no solvent residue on the processed solid and the isolation and recovery of solute and solvent for reuse can be fulfilled upon a simple mechanical expansion to atmospheric pressure. However, the high-pressure operation means an increase in the capital investment, which might limit its use in some applications. In both aqueous surfactant washing and $SCCO_2$ extraction processes, the cleaning efficiency for a batch of grinding sludge is determined by the residual oil and phosphorus contents in the treated solid matrix.

Aqueous Washing Process

Many bench-scale and pilot studies have shown promising results of using aqueous solutions of commercially available surfactants to solubilize and remove hydrophobic organic contaminants and oil from certain solid matrix. This cleaning technology has been successfully implemented in several soil washing projects for remediating contaminated soils (1-7).

The aqueous surfactant-based cleaning process described in this work is technically similar to soil washing in that the major objective is to remove an organic contaminant (cutting oil) with the water-soluble phosphorus additive from a fine solid material. In our lab, we have examined a process which involves the use of aqueous-based surfactant washing for reclamation of alloy steel powder contaminated by grinding lubricant. The process flow diagram of the washing operation is depicted in Figure 1. The oily grinding sludge will be lifted to a hopper that will feed a washing tank. The batch of the solid being washed is stirred vigorously in the tank while washing solution flows continuously through the waste. After a certain washing time, the wet clean solid next goes to a rinse tank and from there to a solid separation unit. The focus of this work is on the washing step and thus the subsequent solid treatment process will be described in a separate paper. In aqueous cleaning, the contaminated water generated in the process must be treated to recover oil and surfactant. For instance an oil-water separator might be used to skim the free oil with a plate separator, followed by an ultrafiltration treatment to separate oil from the surfactant solution. The ultrafiltration system is used to break the oil-aqueous phase emulsion that results from the washing step. A portion of the clean washing solution would be returned to the inlet of the washing process, while a take-off stream would be sent to a public water treatment system.

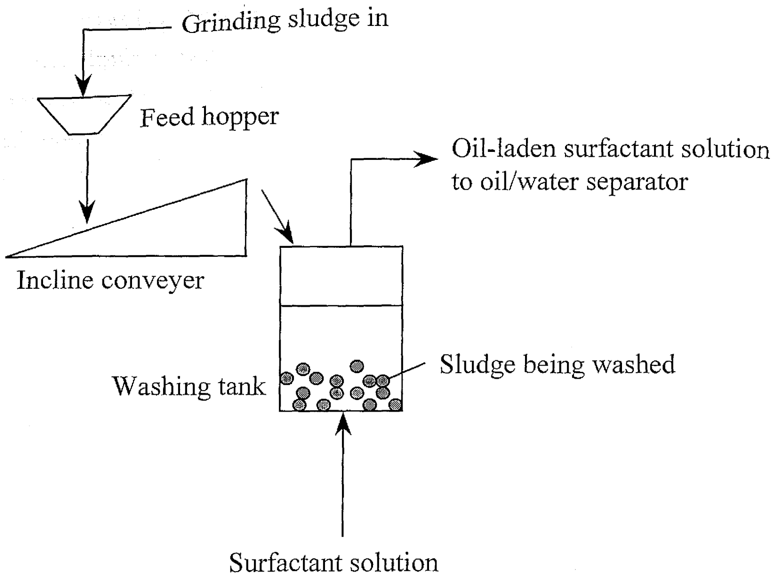

FIGURE 1. Process flow diagram of washing operation for recycling grinding sludge.

$SCCO_2$ Extraction Process

$SCCO_2$ extraction has been extensively studied for its application in the regeneration of contaminated adsorbents, and has been promoted for soil remediation and parts cleaning (8-13). It is considered promising for selected hazardous waste cleanup projects. Adkins *et al.* (12) investigated the feasibility of using $SCCO_2$ extraction to segregate hazardous oils, greases, and organic solvents from non-hazardous debris such as rags, wipes, swabs, etc., and the overall results were promising technically and economically. For our present study, bench-scale supercritical extraction was conducted to determine the efficient operating conditions for oil removal. An additional objective of our research is to determine whether the phosphorus component contained in the cutting oil can be extracted with dense CO_2.

Figure 2 is a process flow diagram of $SCCO_2$ extraction system for cleaning and recycling grinding sludge. The solvent (CO_2) flows through the solid waste bed confined in an extractor, dissolving and removing the solute (cutting oil and phosphorus additive)

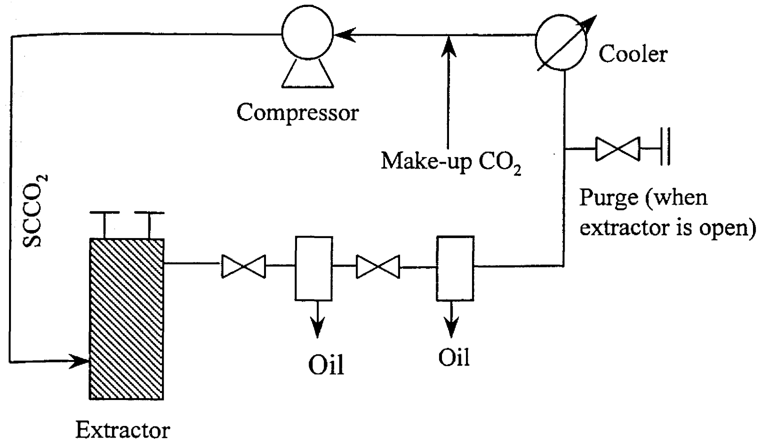

FIGURE 2. Process flow diagram of $SCCO_2$ extraction system for recycling grinding sludge.

adhering to the solid matrix. The contaminant-laden fluid is then mechanically depressurized and the oil and phosphorus will precipitate from the fluid; thus the separation of the solvent from the contaminants will be accomplished, and cutting oil will be left to be collected and shipped to the oil producers. The used CO_2 would then be captured, pressurized and recycled to the inlet of the extractor along with the make-up CO_2. Once the oil is removed, only the metallics and non-metallics will remain in the solid matrix, which will be subjected to additional treatment to recover alloy steel from the non-metallic solids.

EXPERIMENTAL AND THEORETICAL STUDY OF AQUEOUS CLEANING

The washing process requires the use of a specialty surfactant package that will enhance the wetting ability and the detergency of the washing solution by reducing the surface tension of the aqueous phase and by acting as a detergent. The efficiency of aqueous surfactant washing is primarily determined by the surfactant's ability to disperse, transport, solubilize, and thus remove the nonpolar contaminant from the solid matrix. Surfactants have the tendency to reduce the surface tension of the aqueous solution, which will benefit the transport of the contaminant molecules. In addition, as the surfactant concentration approaches the critical micelle concentration, the surfactant monomers will aggregate to form micelles with hydrophobic cores, and these nonpolar interiors may dissolve substantial quantities of nonpolar solutes. Therefore, in general, surfactants enhance the contaminant removal from the solid matrix by two mechanisms, mobilization and solubilization.

Experimental Results

Small-scale batch washing has been performed to test the feasibility of using aqueous surfactant washing techniques to remove oil with phosphorus additive from the solid waste. Since the efficiency of the washing technique is evaluated by the residual oil and phosphorus contents in the treated solid waste, the accuracy of the residual oil analysis is essential. It should be noted that the cutting oil (which is petroleum-based) was treated as a pseudocomponent with the properties of normal decane ($C_{10}H_{22}$). Three different methods were employed for the oil analysis: Total Organic Carbon (TOC), Total Recoverable Petroleum Hydrocarbon (TRPH), and a gravimetric method. TOC is a standard analytical method based on combustion of carbon to CO_2. The oil concentration of the sample then can be calculated by converting the organic carbon analysis to oil content with the assumption that all organic carbon is in the form of $C_{10}H_{22}$. We have chosen TOC to be the analytical method for our swarf samples as it gives the most consistent results.

Because of the key role a surfactant plays in dispersing and solubilizing contaminant molecules, the efficiency of aqueous washing techniques depends strongly on the selection of a suitable surfactant. Our experiments have been focused on testing various commercially available surfactant packages that have been successfully used in different industrial cleaning processes, which include Micro™ (International Products Corp., Burlington, NJ), AquaTek® (Rhone-Poulenc, Cranbury, NJ), and SA8® (Amway Corp., Ada, MI). Our experimental results show that the phosphorus content can be easily reduced before a sufficient oil removal is obtained, due to the water-soluble but not very oil-soluble nature of the phosphorus additive. Therefore, the success of the aqueous cleaning technique is decided mostly by its ability to remove oil from the solid matrix.

In our bench-scale experiments, none of the surfactant solutions tested could wash grinding sludge to an acceptable level of oil in a single 15-minute washing. Several cycles of the washing step were needed to obtain the desired cleanness for the recyclable product. Table 1 displays the washing results of a sample which originally contained 21.23 wt% of oil. Out of the three surfactants tested, only SA8 removed sufficient oil from the waste (86% oil removal) and yielded an acceptable sample after a reasonable number of washings.

A Mass Transfer Model for Aqueous Surfactant Cleaning

In a semi-continuous cleaning process (Figure 1), the small solid particles are confined in a well-stirred tank (treated as a single compartment) and are washed by a continuous flow of oil-free surfactant solution that is charged into the tank from the bottom (14). Assuming that the mass of (oil-free) solid is constant during the washing process, as is the volume of surfactant solution in the washing equipment, then the total mass of oil (considered as a single component) in the tank can be described by

$$M_t = m_t W + M_{oil} C_t V \qquad Eq.(1)$$

where C_t (mol oil /L solution) is the cutting oil concentration in the solution, m_t (g oil/ g solid) is the oil concentration in the solid matrix, M_t (g) is the total mass of oil in the tank, M_{oil} is the molecular weight of oil, and V is the volume of the solution in the tank.

The diffusional transport of oil from the interiors of the solid can be represented by a mass transfer equation:

$$\left(\frac{dm_t}{dt}\right)_{diff} = \lambda(m_t^e - m_t) \qquad Eq.(2)$$

where m^e (g oil/g solid) is the equilibrium concentration of oil in the solid matrix, and λ (s^{-1}) is the overall mass transfer coefficient within the solid matrix. The value of λ can be

TABLE 1. ANALYTICAL RESULTS FOR WASHED SAMPLES

Surfactant Used	Numbers of Washings	TOC (wt%)	Residual Oil Content (wt%)
Micro	1	14.12	16.94
	3	8.71	10.45
	6	5.58	6.69
Aqua-Tek	3	9.90	11.88
	5	6.36	7.63
SA8	3	2.44	2.93

estimated by the following equation that is developed using a lumped parameter approach (14):

$$\lambda = \left(\frac{\pi}{R}\right)^2 D \qquad Eq.(3)$$

where R is the effective radius of the waste particles, D (m^2/s) is the effective diffusion coefficient that characterizes the internal diffusion of oil and its value is obtained from the literature (2).

Eq. (2) is integrated over a time increment Δt that is comparable in magnitude to $1/\lambda$ to yield:

$$m_{t+\Delta t} - m_t = (m_t^e - m_t)[1 - \exp(-\lambda \Delta t)] \qquad Eq.(4)$$

Therefore the oil transport can be described by

$$\frac{dm_t}{dt} = (m_t^e - m_t)\frac{[1 - \exp(-\lambda \Delta t)]}{\Delta t} \qquad Eq.(5)$$

Combine Eqs. (1) and (5) to obtain the equation for oil transport in the aqueous phase:

$$\frac{dC_t}{dt} = -\frac{Q}{V}C_t - \frac{W}{M_{oil}V}(m_t^e - m_t)\frac{[1 - \exp(-\lambda\Delta t)]}{\Delta t} \qquad Eq.(6)$$

Assuming that at equilibrium a linear relationship exists between the cutting oil concentrations in the aqueous and solid phases

$$C_t^e = Km_t^e \qquad \text{Eq.}(7)$$

where K is the isotherm constant which has the unit of mol/L. The value of K is determined in small-scale batch operations where the distribution of oil can reach equilibrium between the aqueous and solid phases (14).

Eqs. (1), (3), (6) and (7) can be solved simultaneously using numerical integration to obtain the dynamic response of the oil concentration histories in the surfactant solution and in the solid waste during the washing process. The parameters used in the mass transfer model are listed in Table 2.

The theoretical curves are plotted for a 60-minute washing process. Figure 3 shows the influence of the waste particle size on oil removal efficiency. When the effective radius of the particle is reduced from 1.5×10^{-3} to 1.0×10^{-3} m, the residual oil content in the solid matrix is reduced by approximately 40%. If the particle size is further reduced to 0.5×10^{-3} m, the oil content then is reduced by another 40%. In general, a fine pre-washing pulverization is an effective way to increase oil removal efficiency, but this operation would increase processing costs.

EXPERIMENTAL AND THEORETICAL STUDY OF SCCO$_2$ EXTRACTION PROCESS

The advantages of using SCCO$_2$ as a solvent, namely, its nontoxic, nonflammable nature, and its low critical temperature and pressure, are already widely recognized. In addition, applying this technology to this solid waste cleaning project can eliminate the

TABLE 2. MODEL PARAMETERS FOR SEMI-CONTINUOUS AQUEOUS WASHING PROCESS

Parameters	Parameter Values
Linear isotherm constant, K	0.0960 L/mol
Initial oil concentration in sludge, m(t=0)	0.2123 g oil/g solid
Effective diffusion coefficient of oil, D	10^{-10} m^2/s
Effective radius of sludge particles, R	0.5×10^{-3}, (1.0×10^{-3}, 1.5×10^{-3}) m
Inverse time constant for diffusion, λ_1	0.00394, (9.86×10^{-4}, 4.38×10^{-4}) s^{-1}

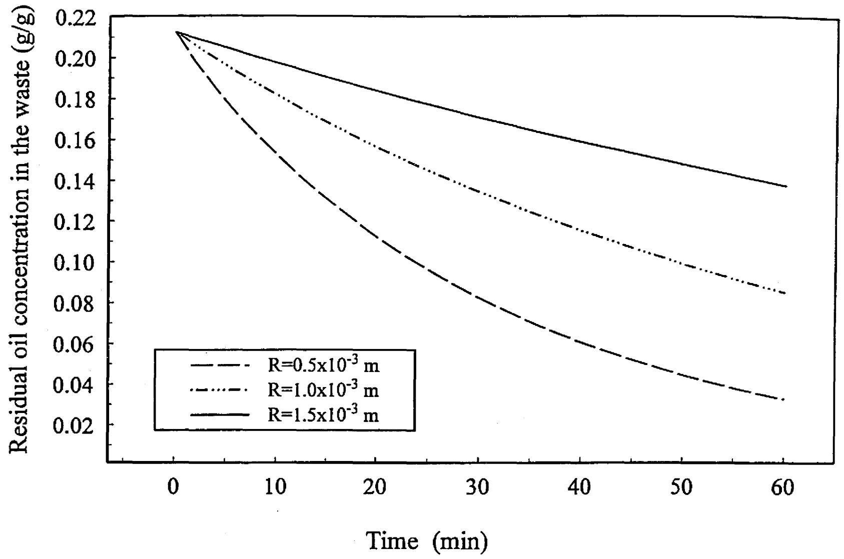

FIGURE 3. Effect of particle size on oil concentration history in grinding sludge during aqueous cleaning process.

production of large quantity of contaminated water as well as the need for expensive surfactant packages. The mechanism of $SCCO_2$ cleaning is driven primarily by the solubility (a thermodynamic equilibrium property) and extractability (a mass transfer factor) of the cutting oil and phosphorus additive. These contaminants are leached from the solid matrix and dissolved into the mobile phase due to the increased solvating power of CO_2 at a temperature and pressure above its critical point.

Experimental Results and Discussion

The bench-scale apparatus used to run the semi-continuous extraction experiments is shown in an earlier paper (14), and a gravimetric method was developed to determine the residual oil concentration in the extracted samples, where the sample weight loss during the extraction process was considered due only to the oil removal. Because of the low phosphorus content in this particular kind of grinding sludge (<0.03 wt%), it was reasonable to assume that the weight loss due to phosphorus removal was negligible. The analysis of the residual phosphorus content in the solid matrix was done by Galbraith Laboratories (Knoxville, TN).

The extraction was first run to find the suitable operation conditions for this sludge cleaning. Our experimental results revealed that a standard extraction procedure (U.S. EPA Method 3560) was very efficient in removing cutting oil from the solid. This procedure was originally developed for Total Recoverable Petroleum Hydrocarbon analysis, and it recommended a 30-minute extraction process at 340 atm and 80 ^{0}C (15). Note that in a supercritical region, the temperature and pressure affect the density and viscosity of the fluid phase significantly, and both the density and viscosity may have a strong effect on the extraction efficiency. Increasing the pressure or lowering the temperature will result in higher density and viscosity. While a higher density may enhance the solubility of a solute in the fluid phase, higher viscosity will have a negative effect on the solute diffusion rate and thus an adverse effect on the solubility of the solute (16, 17). In general, at pressures near the critical point, the fluid density is a dominating factor and thus a lower extraction temperature in the liquid-phase region is preferred. At an operating pressure significantly higher than the critical point, both the density and viscosity of the fluid phase are important factors for extraction efficiency. At an even higher pressure, the viscosity effect will become dominating where higher temperature increases the extraction efficiency (16, 17). The pressures chosen for our experiments were much higher than the critical point of CO_2; therefore the optimum extraction temperature should lie in the supercritical region. Table 3 summarizes some of the experimental results. The data showed that increasing the pressure by a multiple of 2.5 (from 136 to 340 atm) and lowering the temperature from 100 to 80 ^{0}C resulted in a significant increase in oil removal (from an average removal of 25.3% to 68.1%), even though the extraction time was shortened from 90 to 30 minutes. This shows that even at the pressure of 136 atm, the density of CO_2 phase still significantly affects the solubility of cutting oil and consequently the extraction efficiency. However, without more experimental data and sufficient theoretical studies, no general rules can be developed to obtain optimum extraction temperatures and pressures for removing cutting oil from grinding sludge.

Additional experiments were performed to confirm that EPA Method 3560 was sufficiently efficient in removing phosphorus additive from grinding sludge, or whether further cleaning was necessary. To confirm, three CO_2-cleaned samples were mixed together and then divided into thirds. The first sample received no further cleaning. The second one was washed with pure water, and the third was washed with aqueous solution of Micro^{TM}. The residual phosphorus contents in these three samples are shown in Table 4. It is evident that a 30-minute extraction at 80 ^{0}C and 340 atm could remove phosphorus to an acceptable level and that within experimental error the further aqueous washings did not show any additional phosphorus removal.

Although EPA Method 3560 was an effective method to remove cutting oil and phosphorus additive from the samples, a 30-minute extraction was not long enough to clean swarf to an acceptable oil level (<5 wt%). Therefore the extraction time was increased to 60 minutes, but the extraction temperature and pressure were kept at 80^{0}C and 340 atm. Some dynamic data were also obtained to show the history of oil concentration in the solid sample during a 60-minute extraction process (Figure 4). More experiments were performed to prove that at bench-scale and 340-atm extraction pressure, the oil extraction efficiency was independent of solvent flow rate (14). This result was consistent with the conclusion drawn by Dahmen *et al.* (18), who investigated the feasibility of using $SCCO_2$ extraction to clean metal cutting waste contaminated with high oil content.

TABLE 3. ANALYTICAL RESULTS FOR EXTRACTED SAMPLES

Batch of sludge	Pressure (atm)	Temp. (^{0}C)	Density (g/ml)	Time (min)	Residual Oil Content (wt%)	Oil Removal (%)
1 (untreated)					21.2	
2	136	100	0.294	90	16.2	23.6
3	136	100		90	15.5	26.9
4	340	80	0.785	30	6.7	68.4
5	340	80		30	8.2	61.3
6	340	80		30	5.4	74.5

TABLE 4. RESIDUAL PHOSPHORUS CONTENTS IN VARIOUS SAMPLES

Sample	Residual Phosphorus Content (wt%)
Extracted with $SCCO_2$	0.014
Extracted with $SCCO_2$ and washed with H_2O	0.016
Extracted with $SCCO_2$ and washed with Micro solution	0.015

Mathematical Modeling for $SCCO_2$ Cleaning

The extraction is conducted using a fixed bed of spherical particles of the oily waste, with an initial concentration of adsorbed solute (oil) q_0. The solid bed is viewed as well mixed with efficient contacting by CO_2. In our earlier work, an irreversible desorption model has been used to simulate the bench-scale $SCCO_2$ extraction. The mass balances in the bulk and solid phases in the extraction cell are described by the following equations:

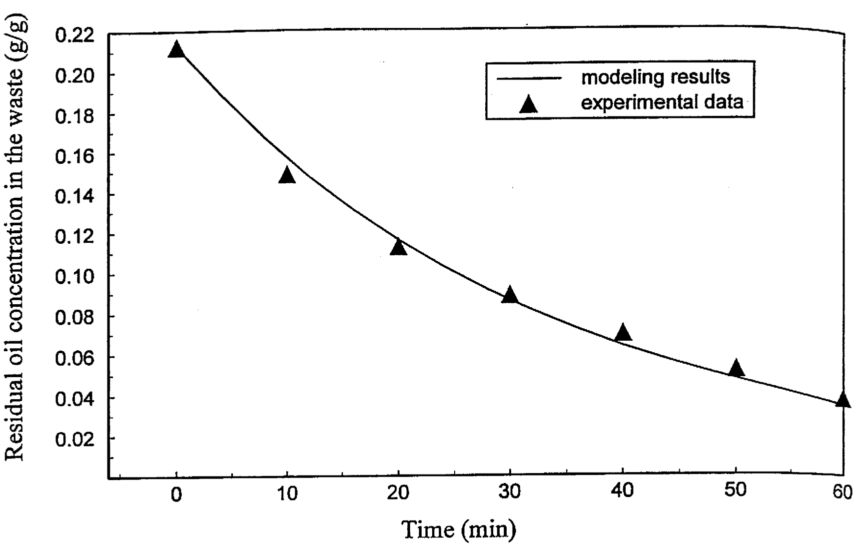

FIGURE 4. Oil concentration history in grinding sludge during SCCO$_2$ extraction process.

$$\frac{dC}{dt}+\frac{uC}{\varepsilon V_{bed}}+\frac{1-\varepsilon}{\varepsilon}\rho\frac{dq}{dt}=0 \qquad \text{Eq. (8)}$$

$$\frac{dq}{dt}=-k_d q \qquad Eq.(9)$$

where C (g oil/ml of fluid) is the cutting oil concentration is the mobile fluid phase, q (g oil/g solid) is the oil concentration in the machining waste, ρ is the density of the waste (g/ml), V_{bed} (ml) is the volume of the solid waste bed (including void volume), ε is the void fraction of the bed, and k_d (min^{-1}) is the desorption rate constant which is determined by fitting the experimental data into the modeling equations. This model presumes that the solvent flow rate has no influence on oil desorption (i.e., oil concentration decay rate in the solid phase), and consequently the desorption profile is only a function of k_d. The parameters used in this model are summarized in Table 5.

TABLE 5. MODEL PARAMETERS FOR $SCCO_2$ EXTRACTION PROCESS

Parameter	Parameter Value
Desorption rate constant, K	$0.030\ min^{-1}$
Density of raw grinding sludge, ρ	2.6 g/ml
Volume of the solid bed, V_{bed}	8.0 ml
Void fraction of the solid bed, ε	0.3

Figure 4 displays the oil concentration histories in grinding sludge during a 60-minute extraction, and the modeling results are compared with the experimental data. With the calculated k_d, the modeling results match well with the experimental data under our operating conditions. It should be noted that although the irreversible desorption step is a limiting factor which primarily controls the cleaning efficiency, the desorption would be limited by the equilibrium distribution of oil between the adsorbent and $SCCO_2$ in the absence of mass transfer resistance.

CONCLUSIONS

The feasibility of using either aqueous surfactant washing or $SCCO_2$ extraction to remove cutting oil with phosphorus additive from grinding sludge was tested. Under suitable operating conditions, the bench-scale experiments showed promising results with both separating and cleaning techniques.

The efficiency of aqueous washing depends on the selection of a suitable surfactant. The removal of phosphorus by aqueous washing was proved to be easier than that of oil because of its water-soluble nature. A surfactant developed for industrial cleaning, SA8, removed 86% of the oil from grinding sludge in three 15-minute batch washings and was recommended for a pilot plant test. A semi-continuous washing process, which would be more suitable for larger-scale applications, was studied using a mass transfer model. In $SCCO_2$ extraction, the efficient extraction temperature and pressure for cleaning grinding sludge were found to be 80 ^0C and 340 atm. At the pressure of 136 atm, the density of the fluid phase was a dominating factor for the solubility of cutting oil. However, no more detailed conclusions could be drawn without more experimental data. Both phosphorus and oil removal within a 60-minute extraction were sufficient to produce a batch of recyclable grinding sludge. The residual phosphorus content in an extracted sample was 0.015 wt%, and a further cleaning with aqueous washing did not result in any higher phosphorus removal. The oil concentration in an extracted sample was approximately 3.5 wt% that also met the recycle requirement. An irreversible desorption model was used to describe the extraction process, and the simulated results matched very well with the experimental data.

Ultimately the selection of a separation process for recovering alloy steel from grinding sludge will depend on the economic situation of the project. A subsequent paper will present the economic analysis based on these technical results, and will illustrate the importance of landfill management on the commercial feasibility of cleaning and recycling grinding sludge.

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