

Innovative Hydrometallurgical Method for Recycling Steel Swarf

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Abstract

Due to its high concentration of heavy metals and cutting fluids, steel swarf is a hazardous waste that is difficult to recycle and is typically landfilled today. The swarf, which can have an iron content of up to 80%, is a possible secondary raw material for the synthesis of reagents like ferric chloride, which are used in the treatment of wastewater [1-15]. In this study, a novel hydrometallurgical method for selectively separating iron from heavy metals and producing ferric chloride from recycled steel swarf is presented. Hydrochloric acid was used to leach swarf that contained 69 percent iron. The result was a leachate with 24.600 mg/L Fe, 150 mg/L Mn, 12 mg/L Ni, and 1 mg/L Cr and Mo. With barely 1% solubility in the solid waste, the oil-based cutting fluids primarily remained.

Introduction

Large quantities of ferrous swarf and other non-ferrous byproducts are produced during the machining of steel items. Although it is uncertain how much steel swarf is produced annually, it has been estimated to be between 2.3-5.8 million tonnes. Cutting fluids are frequently used during operations like milling, turning, and grinding to lubricate and cool the metalworking machinery and produce swarf that is covered in oil, (1996a). Steel manufacturers are hesitant to handle this swarf as waste because flammable lubricants can cause explosions and flames that harm processing machinery. Additionally, phosphorus and sulphur are sometimes found in cutting fluids, which can negatively impact the steel that is produced. Due to the low economic viability of recycling metals from oil-covered swarf, swarf).

Swarf produced during grinding operations has a particularly complex makeup since it includes grinding wheel binder material in addition to cutting fluids and abrasives. Iron, which makes up between 50 and 80 percent of this swarf, is its primary component. Along with iron, it may also include different steel alloying components like Cr, Mn, and Mo, as well as 4–20 percent of ceramic abrasives like alumina or silicon carbide. Cutting fluids can have a variety of additives, such as biocides, rust inhibitors, and severe pressure agents, and they can be synthetic or mineral oil-based. Numerous additives lack biodegradability and are hazardous. Because of this, the European Union considers cutting fluids to be hazardous waste (European Waste Catalogue, 12 01 07*). Partial dissolution possible through filtration, magnetic separation or centrifugation.

Previous studies on recycling of swarf have primarily been focused on lowering the cutting fluid content. Extraction of the cutting fluids using supercritical carbon dioxide and aqueous washing of swarf with surfactants has so far received most attention. With these techniques, the cutting fluid content can usually be reduced below 5% which enables reprocessing of the swarf as scrap. Recently suggested washing swarf with alkaline surfactants and mechanically separating the ferrous fraction from abrasives. With this approach, new steel can be produced directly by sintering the metallic swarf. Moreover, abrasive material could potentially be reused instead of ending up as slag at the steel mill. Steel produced by sintering however had low quality due to difficulties in separating swarf from abrasives.

Recycling of swarf using a hydrometallurgical approach has not yet been reported. Hydrometallurgy offers an energy efficient alternative to pyro metallurgical processes and can be used to recover metals from low grade ores and secondary resources. This technique has already seen application in recycling of other by products from the

steel industry. While most studies have been focused on the recovery of Zn from electric arc furnace dust, recycling of valuable alloying elements like Mo and W has also recently gained some attention. Hydrometallurgy could potentially be used to selectively extract metals from swarf since oil-based cutting fluids have a low solubility in water.

Subjective Heading

The aim of this work was to achieve selective separation of metals from cutting fluid and abrasives by leaching. For this purpose, swarf was leached with dilute hydrochloric acid solutions while maintaining specific pH levels. This method has been applied previously for decontamination and recycling of a variety of different wastes like soils, MSWI ashes, flue dusts and slags. Hydrochloric acid can react with metals to form soluble chloride salts and since steel swarf has a high iron content, it can represent a raw material for production of ferric chloride (FeCl_3). Solutions of FeCl_3 are a marketable product and can be used as flocculants in wastewater treatment. By providing an alternative application for the swarf, its potential value is increased. This promotes recycling and makes landfilling less attractive and thus brings a more sustainable solution for its handling. Lowering the content of cutting fluid has been the main focus of earlier investigations on recycling swarf. Most research has been focused on supercritical carbon dioxide extraction of cutting fluids and aqueous swarf washing with surfactants these methods enable the recycling of the swarf as scrap by typically lowering the cutting fluid level below 5%. Recently advised mechanically extracting the ferrous portion from abrasives and cleaning swarf with alkaline surfactants. By sintering the metallic swarf, new steel can be made using this method. Additionally, abrasive material could be recycled rather than becoming slag.

Discussion

By washing swarf samples with toluene (99.5 percent, Sigma-

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Aldrich, ACS reagent), heptane (99 percent, Sigma-Aldrich, Reagent Plus and ethanol in successive phases, the amount of cutting fluid was determined (95 percent, Solvaco, Analytical grade). Swarf (2 g) was put to volumetric flasks, cleaned, and then mixed by shaking for 5 minutes while flasks were filled with an organic solution (50 mL). After one hour, after the suspended solids had settled, the liquid phase was decanted, bringing the washing stage to a close. Toluene was used to first wash the swarf in two stages in order to dissolve the cutting fluids. To remove the toluene, three stages of washing with heptane were followed by three stages of ethanol. Glass microfibre filters (1.6 m pore size, Whatman, GF/A grade) and filter sheets with solid particles were used to filter the final ethanol solutions.

By washing swarf samples with toluene (99.5 percent, Sigma-Aldrich, ACS reagent), heptane (99 percent, Sigma-Aldrich, ReagentPlus, and ethanol (95 percent, Solvaco,) in successive phases, the amount of cutting fluid was calculated. Using X-ray diffraction, the crystalline compositions of swarf and leaching wastes were determined (XRD, Bruker, D8 advance). A 2 angular range between 10° and 90°, a step size of 0.04°, and a wavelength of 1.5406 were used to evaluate the samples. The International Center for Diffraction Data (ICDD) database was used to compare diffraction peaks. In jacketed 200 mL glass reactors, leaching studies were carried out in pairs. Leaching temperatures were managed by controlling the flow of hot water from a bath to the outer reactor shells. Both reactors used polypropylene burettes with anti-diffusion filters for titrations and glass electrodes for pH measurement. with electric stirrers the swarf in leaching media that is buoyant and oily. Both reactors' electrodes and burettes were attached to an automatic titrator (Metrohm, Titrando 905). Tiamo™ was used to configure the titrator to monitor and regulate the pH of leaching solutions. Every time the pH exceeded the intended threshold, 10 mL dosage units of titrant were delivered. To prevent dilution of the leaching media, a 5 M HCl solution was utilised as a titrant.

Design of experiments (DOE) and response surface approach were used with MATLAB computations to optimise the leaching procedure. Montgomery provides a thorough explanation of these techniques (2020). In order to prevent severe circumstances in axial points, experiments were carried out using a face centred composite design. To calculate the experimental error, four replicates of the central point were employed. Every experiment was run in a random order, and experimental pairings received random reactor assignments. Temperature (x1), pH (x2), and solid to liquid (S:L) ratio effects were examined (x3). Table 2 lists the factor values that were chosen based on the outcomes of preliminary leaching experiments and Eh-pH diagrams. Based on how long it took Cr to reach a constant concentration in earlier leaching tests, the leaching time was chosen at 3 hours. Fe, Mn, Ni, Cr, and Mo contents in the leachate were measured, and Eq was used to compute the leaching efficiency responses. Efficiency data for Fe, Cr, Mn and Ni was used to fit linear second order regression models with two- and three-way interaction terms, using the least squares method. The significance of regression models and regression coefficients was evaluated with hypothesis testing on 95% confidence bases and adjusted coefficients of determination (Radj2) were used to evaluate goodness of fit. Regression models were used to plot response surfaces for two factors while keeping one factor at a constant level.

Table 2 lists the experimental conditions and results from the experimental design. The base 23 factorial design is represented by experiments 1 through 8, centre point experiments 9 through 12, and axial points 13 through 18 of the FCC. The stability of FeCl₃ was used to determine the temperature and pH values. Eh-pH diagrams show

that FeCl₃ is stable at 60 °C below pH 4.2. In tests 4 and 8, some Fe precipitation was seen as a result of operating close to the stability limit at high temperature and pH values. In order to prevent the viscosity of the leaching media from decreasing, which could prevent the mixing and distribution of HCl, relatively low ratios were used for the design.

Al₂O₃ has a number of minor peaks that may be seen at 25.4°, 35.0°, 37.7°, 57.4°, 66.4°, 68.1°, 76.5°, and 80.8°. This is more evident when compared to Fig. 1b, which shows that the majority of the solid residues discovered to contain alumina abrasives after being dissolved in aqua regia. A second, smaller peak with a spinel structure, corresponding to aluminium oxides, can be seen at 18.1° in Fig. 1b (MxAlyO₄). This most likely result from abrasive impurities. Abrasives made up about 6 wt percent of the entire material. A bump between 10 and 20 degrees can be seen. This bump is likely caused by the amorphous cutting fluid. Most of the cutting fluid was oxidised when swarf was dissolved in aqua regia, but some was left on the abrasive. Leaching residues comprised 28 wt% carbon, according to combustion analyses.

In conclusion, the swarf had a high Fe concentration and might serve as a source for iron chloride manufacturing. There was no proof that it had oxidised Fe in it. In addition to Fe, the swarf also contained smaller levels of Cr, Mn, Mo, and Ni, all of which were soluble in aqua regia, as well as Al₂O₃, which was insoluble. The cutting oil was primarily responsible for the relatively high carbon content. The oil was quite tenacious and Metallic Fe, the primary component of the swarf, can react with HCl to produce iron chlorides using equations $2\text{Fe} + 2\text{HCl}(\text{aq}) \rightarrow \text{FeCl}_2(\text{aq}) + \text{H}_2(\text{g})$.

These reactions, which have Gro values of 21.8 kJ/mol and 11.4 kJ/mol respectively, are reversible and non-spontaneous in contrast to the dissolution of metallic Fe. High temperatures and low HCl concentrations enhance the precipitation of FeCl₃ via the reverse reactions. FeCl₃ is stable below pH 5 at 25 °C, with a diminishing stability at higher temperatures, according to Eh-pH graphs.

Table S1 contains the ANOVA findings for the regression models. F-tests (= 0.05) were used to assess the significance of regression models and the presence of lack of fit (LOF). The significance of each regression model (F>Fcrit) was high. The model for Ni contained some LOF, but it was made better by removing least significant terms from the regression model until the LOF was minimized. Figure S1 provides Pareto diagrams with standardised regression coefficients. T-tests were used to determine the significance of the coefficients (= 0.05). The leaching of Fe was most affected by temperature (x1), pH (x2), and S:L ratio (x3), while temperature (x1) and pH (x2) had the largest impact. The Pareto chart for Mn and Fe were nearly identical. The regression models for Fe and Mn were similar, as shown by a comparison of and Therefore, while leaching Fe, co-leaching of Mn is inevitable. Ni leaching was mostly affected by x1 and x2, although x3 also had a considerable impact. This offered a chance to regulate Ni oxidation without significantly impacting Fe leaching. Leaching of Cr was unrelated.

Optimization of the leaching process was accomplished with response surface methodology. Response surfaces were created by calculating leaching efficiencies using the regression models in at different temperature and pH levels while keeping the S:L ratio constant at the low (x₃ = -1), intermediate (x₃ = 0) and high (x₃ = 1) levels. Contour plots of response surfaces are given.

Contour plots for Fe in a-c show that leaching efficiencies close to 100% were generally achievable within 3 h between pH 2-3 and 40 °C-60 °C. A maximum in leaching efficiency was predicted at 50 °C and pH

levels between 2 and 2.5, depending on the S:L ratio. When increasing the S:L ratio, the ratio of metals to acid increases which can limit reaction kinetics. This behavior was also observed when comparing pH levels in the preliminary tests in and explains the relatively low efficiencies for Fe at pH 4 and 20 °C after 3 h.

Leaching rates and efficiencies for Fe could be improved by operating at a higher temperature. Contour plots show that predicted efficiencies at pH 4 were generally 50% higher when operating at 60 °C compared to 20 °C. Likewise, at pH 2 only 80% of Fe could be leached at 20 °C while efficiencies were 100% at temperatures above 40 °C. According to the preliminary test in a, the Fe concentration reached a steady level after 3 h at pH 2 and 25 °C. This implies that only 80% of Fe was leachable when operating at 20 °C. Remaining Fe was likely trapped in the solid residue with Cr. Chromium oxides act as stabilizers in steel and are impervious to dilute HCl solutions.

Leaching of Ni was highly temperature dependent which is clear from the steep efficiency gradient. The leaching process was optimized using the response surface approach. Leaching efficiencies at various temperatures and pH levels were calculated using the regression models in, while maintaining a constant S:L ratio at the low ($x_3 = 1$), intermediate ($x_3 = 0$), and high ($x_3 = -1$) levels. Figure 3 provides contour maps of the response surfaces. Between 20 °C and 40 °C in g-i. Maximum leaching efficiencies were predicted at 50 °C and pH 2. Comparing contour plots for Ni shows that S:L ratio also had a relatively high effect. The regression model for Ni in, shows that leaching of Ni decreased linearly with x_3 and predicted efficiencies for Ni were generally 25–30% lower at 1:20 than 1:50 g/mL.

Conclusion

The leaching process was optimised by comparing contour plots. According to preliminary testing shown in Fe could often be leached with high efficiency given enough time. Since Mn's leaching behaviour was identical to that of Fe's, it was not taken into account during optimization. Therefore, reducing Cr and Ni co-leaching was of the utmost importance.

Cr leaching was limited at pH 4 and 60 °C. Although working at a high temperature encouraged the leaching of Ni, the swarf contained far less of this metal. The rate and effectiveness of leaching for Fe were likewise enhanced by high temperatures. Leaching of Ni at 60 °C and pH 4 was reduced by operating at 1:20 g/mL. At this S:L ratio as opposed to 1:50 g/mL, predicted efficiency for both Fe and Ni were 25 percent lower. There was no proof that the S:L ratio had an impact on the leachability for Fe, although this was explained by restrictions in reaction kinetics. However, regardless of pH or temperature, efficiency for Ni typically declined as S:L ratio increased. According to thermodynamic calculations, the production of NiCl₂ from Ni and HCl react spontaneously with a ΔG of 45.8 kJ/mol, and Ni²⁺ is stable at 60 °C below pH 4.7. There is no data to suggest that Ni is more difficult to leach than Fe when compared to the ΔG for Fe. However, it

is clear that in a battle for HCl, Ni is less advantageous than Fe. A better pre-concentration of FeCl₃ is also produced when operating at high S:L ratios, which is beneficial from an industrial standpoint.

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Conflict of Interest

The authors declare that they are no conflict of interest.

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