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Leaching of non-ferrous metals using a microemulsion in the system sodium dodecyl sulfate–butanol–caproic acid–kerosene–water

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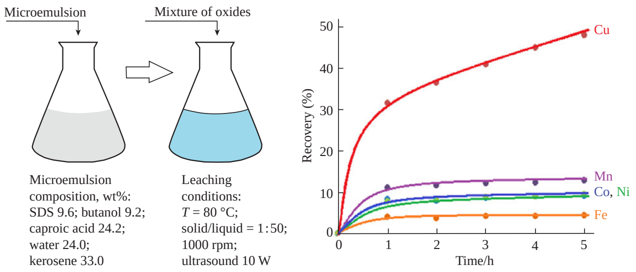
The possibility of using reverse microemulsion based on sodium dodecyl sulfate containing an extractant caproic acid for the selective recovery of non-ferrous metals and their separation from iron in the process of microemulsion leaching has been demonstrated. Using a model system with a mixture of oxides, the following recovery factors of metals are achieved in 5 h of leaching (%): Cu, 47.6; Mn, 12.8; Ni, 9.4; Co, 9.1; Fe, 4.3. When leaching from a sample of oxidized cobalt–copper concentrate, the recovery of metals is as follows (%): Cu, 60.0; Co, 51.3; Mn, 16.5; Fe, 10.0; Ni, 9.3.



Keywords: microemulsion, leaching of metals, non-ferrous metals, sodium dodecyl sulfate, extractant, caproic acid, nanostructured media.

Self-organizing nanostructures of surfactants such as microemulsions (MEs), are promising media for chemical technology, including hydrometallurgy processes.[1–4] The main technological advantages of MEs are their spontaneous formation when mixing the necessary components and the ability to include comparable amounts of polar and non-polar substances, which makes them a ‘universal solvent’. Along with the use of ionic liquids, aqueous biphasic systems and deep eutectic solvents,[5] the use of reverse MEs is considered as one of the modern methods of liquid–liquid extraction of metals.[6] To form MEs, one or more surfactants are introduced into the organic phase in addition to the extractant. During the extraction, the equilibrium ‘reverse ME–aqueous phase’ is established. In some cases, this method makes it possible to improve metal recovery. The main disadvantage of the method is the need to prevent the formation of stable emulsions that impede phase separation.[6] As an example of the application of MEs in hydrometallurgy, we can cite recently published works on liquid–liquid extraction using MEs of vanadium,[7] palladium[8] and rhenium.[9]

In the microemulsion leaching method, compounds of non-ferrous metals are recovered from natural or technogenic raw materials when they are processed with an extractant containing ME. After leaching, the solid phase is separated and the target components are re-extracted from the ME upon the introduction of mineral acid. The main advantage of microemulsion leaching is the selective extraction of target components and their inclusion in microemulsion droplets (extraction) already at the stage of solid phase processing (leaching), that is, the combination of leaching and extraction within one process takes place.[10] Microemulsion leaching can be considered as an alternative to the method of extracting metals from solid phase particles (including ore and secondary raw materials) due to the selective dissolution of their oxides in deep eutectic solvents.[5,11]

The microemulsion leaching method was successfully tested using the example of treating oxidized cobalt–copper concentrate with a reverse microemulsion of sodium bis(2-ethylhexyl) phosphate containing bis(2-ethylhexyl)phosphoric acid as an extractant.[12] Microemulsion leaching of vanadium from vanadium slag using a microemulsion in the system bis(2-ethylhexyl)phosphoric acid–heptane–aqueous NaOH solution is described.[13] For microemulsion leaching, it is promising to use MEs based on surfactants, which are industrially produced in large volumes, such as sodium dodecyl sulfate (SDS). On a model system with CuO, the possibility of leaching of non-ferrous metals using reverse ME in the system SDS–1-butanol–extractant–kerosene–water containing extractants caproic acid and bis(2-ethylhexyl)phosphoric acid was shown.[14] However, the single oxide model system does not allow the study of leaching selectivity.

The purpose of this work was to study the selectivity of leaching of non-ferrous metals and iron using reverse ME in the system SDS–1-butanol–caproic acid–kerosene–water using a model system in the form of a mixture of oxides of non-ferrous metals and iron and an ore sample. Based on the previous studies,[14] a reverse (‘water in oil’) ME with the following composition was chosen for leaching (mol dm^{-3}): SDS, 0.32; 1-butanol, 1.2; caproic acid, 2.0; water, 12.8 (composition in wt%: SDS, 9.6; 1-butanol, 9.2; caproic acid, 24.2; water, 24.0; kerosene, 33.0).[†]

[†] All reagents were pure grade (no less than 95% main substance), lighting grade kerosene (mixture of C_8–C_{15} hydrocarbons, density of 770 kg m^{-3} at 20 °C) was used. The hydrodynamic diameter of ME droplets determined by dynamic light scattering on a Zetasizer Nano ZS device (Malvern, UK) was 7.5 ± 1.3 nm. Since MEs are thermodynamically stable systems, they are formed spontaneously when the necessary components are mixed and can exist with an unchanged composition indefinitely.[1,2] The region of existence of ME in the system SDS–1-butanol–caproic acid–kerosene–water was shown previously.[14]

The selectivity of microemulsion leaching of metals was studied using a model system of Cu^{II}, Ni^{II}, Co^{II}, Mn^{II} and Fe^{III} oxides.[‡] This choice is due to the high prevalence of these non-ferrous metals in ore and technogenic raw materials, often in combination with iron. Previously,[10,12,14] the process of microemulsion leaching was studied using a model system with CuO, a mixture of oxides being not used as a model. Leaching conditions were selected based on previous[3,10,12,14] studies.[§] It was previously shown on a model system with CuO[12] that the leaching of copper in ME containing the extractant bis(2-ethylhexyl)phosphoric acid $(C_8H_{17}O)_2POOH$ occurs with the formation of a medium salt, according to equation (1):

$$CuO_{(S)} + 2\,(C_8H_{17}O)_2POOH_{(ME)} \rightarrow \tag{1}$$

$$\rightarrow Cu[(C_8H_{17}O)_2POO]_{2(ME)} + H_2O_{(ME)},$$

where the indices ‘S’ and ‘ME’ denote a solid phase and a microemulsion, respectively.

It can be assumed that the recovery of metals in ME containing the extractant caproic acid proceeds in a similar way, with the formation of medium salts of caproic acid and the corresponding metals. For divalent metals M, we can write the following generalized equation (2):

$$MO_{(S)} + 2\,C_5H_{11}COOH_{(ME)} \rightarrow M(C_5H_{11}COO)_{2(ME)} + H_2O_{(ME)}. \tag{2}$$

For Fe^{III} this equation will look like this [equation (3)]:

$$Fe_2O_{3(S)} + 6\,C_5H_{11}COOH_{(ME)} = 2\,Fe(C_5H_{11}COO)_{3(ME)} + 3\,H_2O_{(ME)}. \tag{3}$$

The dependence of the recovery of non-ferrous metals and iron on the time of microemulsion leaching for the model system is presented in Figure 1. For Mn, Co, Ni and Fe, the leaching occurs most actively during the first hour, then their concentrations in ME change insignificantly. The copper concentration in ME grows rapidly during the first hour, then it increases at an approximately constant rate throughout the experiment. According to the recovery, metals are arranged as follows: Cu ≫ Mn > Ni ≈ Co > Fe, *i.e.*, selectivity in the extraction of non-ferrous metals compared to iron is observed; copper is best extracted. Within 5 h of the leaching, the following recovery was achieved (%): Cu, 47.6; Mn, 12.8; Ni, 9.4; Co. 9.1; Fe, 4.3. The experiment was carried out for 5 h to demonstrate the selectivity of leaching of various metals within a period of time suitable from a technological point of view. According to the data obtained for a model system with CuO and ME based on sodium bis(2-ethylhexyl) phosphate,[12] equilibrium was achieved in 32 h; such long-term leaching looks unpractical.

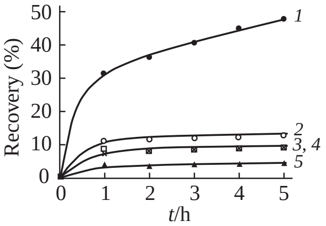


Figure 1 Microemulsion leaching of metals using a model system of oxides: (*1*) Cu , (*2*) Mn, (*3*) Co, (*4*) Ni and (*5*) Fe.

For liquid–liquid extraction of divalent metals using carboxylic acids, a similar selectivity series is known: Cu > Co ≈ Ni ≈ Mn, but Fe^{III} is extracted better than divalent Cu, Mn, Co and Ni.[15] In our experiment, Fe^{III} was recovered worse than divalent metals, which can be explained by the influence of the steric factor. According to equations (2) and (3), salts of caproic acid and the corresponding metals (soaps) are included into the ME; they are localized in the surfactant monolayer at the water–oil interface. Carboxylates of divalent metals contain two hydrocarbon ‘tails’; it is easier for them to be located in a surfactant monolayer so that the polar ‘head’ faces towards the water, and the non-polar ‘tails’ towards the oil phase. For carboxylates of trivalent metals, which have three differently directed non-polar ‘tails’, it is difficult to locate in a surfactant monolayer in ME. It is known, *e.g.*, that the introduction of the trivalent metal salt $La(NO_3)_3$ leads to the destruction of ME in the system sodium bis(2-ethylhexyl) phosphate–1-octanol–toluene–water;[16] in a similar system, sodium salt of naphthenic acid–80 vol% *n*-heptane–20 vol% 2-octanol–water, the introduction of $LaCl_3$, $NdCl_3$ and $EuCl_3$ also leads to destruction of ME.[17]

Figure 2 shows the IR spectra of ME before and after the leaching.[¶] The differences in the spectra are small, since the composition of ME changed slightly. The concentrations of metals in ME after 5 h of leaching were as follows (mol dm^{-3}): Cu, 0.0249; Mn, 0.0086; Co, 0.0052; Ni, 0.0051; Fe, 0.0025. The initial concentration of the extractant was 2.0 mol dm^{-3}; according to equations (2) and (3), its final concentration will be 1.9049 mol dm^{-3}. Thus, the concentration of caproic acid decreased by ~5%, and the corresponding amounts of carboxylates and water were formed, which can explain the slight increase in the intensity of peaks in the IR spectrum of ME after leaching (see Figure 2), *e.g.*, at 3000–3700 cm^{-1} (corresponding to stretching vibrations of OH groups,[18] including water molecules in ME[19]) and at 721–727 cm^{-1} (corresponding to carboxylate ions[18]).

The results obtained on the selectivity of the recovery of non-ferrous metals and their separation from iron were verified during microemulsion leaching of metals from a sample of oxidized cobalt–copper concentrate. The metal content in the concentrate (particle size no more than 0.08 mm) was as follows (g kg^{-1}): Co, 87.0; Cu, 9.4; Ni, 4.0; Mn, 4.1; Fe, 107.0. Main mineral phases in the concentrate (according to X-ray phase analysis) were sodium magnesium silicate Na_2MgSiO_4, triclinic

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To prepare ME, calculated amounts of water, 1-butanol, caproic acid and kerosene were added to a weighed portion of SDS. The components were intensively stirred until SDS was completely dissolved and an optically transparent ME was formed.

[‡] A mixture of metal hydroxides was precipitated from an aqueous solution of their salts with 1 M NaOH solution. The precipitate was washed with distilled water to neutral pH, then dried at 120 °C for 4 h, calcined at 600 °C for 4 h to obtain oxides and crushed to a particle size of <0.08 mm. The concentrations of metals in the model system determined using an Agilent 7900 inductively coupled plasma mass spectrometer were as follows (g kg^{-1}): Cu, 186.2; Co, 163.9; Fe, 98.9; Mn, 209.9; Ni, 207.9.

[§] The leaching process was performed in closed flasks at a ratio of solid to liquid phases S/L = 1 : 50 (volume of the liquid phase was 80 ml) at a combination of mechanical stirring (1000 rpm, heater-stirrer IKA RCT Basic) and ultrasonic dispersing (ultrasonic disperser UZD1-0.1/22, ultrasound power 10 W) at 80 °C. Mixing conditions: paddle stirrer diameter of 25 mm, vessel diameter of 60 mm, Reynolds number of ~1 250 000 (turbulent flow). This mechanical stirring corresponds to a regime in which particles of the solid phase do not settle and the liquid does not splash. During the leaching process the microemulsion was stable and transparent. During the leaching, 2 ml samples of ME were taken, and the metals were re-extracted by mixing ME with a threefold volume of 1 M aqueous HCl solution. After completion of the re-extraction process, the aqueous phase was separated, diluted 10 times with deionized water, and the metal content was determined using an Agilent 7900 spectrometer. Metal recovery (%) was calculated as the ratio of the mass of metal in ME and in a sample of the solid phase, multiplied by 100%.

[¶] IR spectra were recorded at room temperature using a Nicolet 380 FTIR spectrometer (Thermo Scientific, USA) at the Center for Collective Use of Mendeleev University of Chemical Technology of Russia.

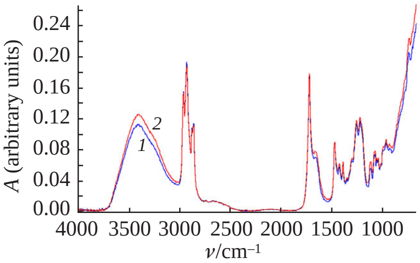

Figure 2 IR spectra of ME: (*1*) before and (*2*) after leaching.

SiO_2, tetragonal SiO_2, ferrosilite $FeSiO_3$, sodium aluminosilicate $Na_6Al_6Si_{10}O_{32}$, and iron silicate Fe_7SiO_{10}. The ME composition, leaching conditions, and metal analysis method were the same as for the model system with oxides. The dependence of the recovery factors of non-ferrous metals and iron on the time of microemulsion leaching is presented in Figure 3.

The results of leaching from cobalt–copper concentrate are similar to those obtained for the model system: active recovery of metals is observed during the first hour, then the process proceeds at an approximately constant speed. Copper and cobalt are best extracted; after 5 h of leaching, the following recovery was achieved (%): Cu, 60.0; Co, 51.3; Mn, 16.5; Fe, 10.0; Ni, 9.3. Accordingly, metals are arranged as follows: $Cu > Co \gg Mn > Fe \approx Ni$, *i.e.*, separation of copper and cobalt from iron, nickel and manganese is observed. Higher values of iron recovery compared to the model system can be explained by the presence of both Fe^{III} and Fe^{II} in the sample. Similar results were previously[12] shown for the leaching of non-ferrous metals from oxidized cobalt–copper concentrate using ME of sodium bis(2-ethylhexyl) phosphate with an extractant bis(2-ethylhexyl)phosphoric acid: after 5 h of leaching, the recovery of Cu was 72%, whereas the recovery of Co, Ni and Fe was 6.0, 5.9 and 0.5%, respectively.

If we consider extractant-containing MEs as an alternative to deep eutectic solvents when these solvents are used for leaching, higher metal recovery can be achieved, but there is no separation of non-ferrous metals from iron. For example, the processing of NdFeB magnets using deep eutectic solvents is described. When they are dissolved in a mixture of choline chloride and lactic acid (1 : 2, mol/mol), the recovery of Fe, Co, B and rare earth elements is 85–97% with a ratio of solid and liquid phases (S/L) of 1 : 50, leaching was carried out at 70 °C for 24 h. At the same time, in the solvents choline chloride/urea and choline chloride/ethylene glycol, the extraction of metals was insignificant. For further separation of Fe, Co, B and rare earth elements, the authors used liquid–liquid extraction.[20] The dissolution of chalcopyrite concentrate in choline chloride/ethylene glycol is described; during 4 h of leaching at 90 °C and S/L equal to 1 : 10, approximately 16% Cu was dissolved; after leaching, the deep eutectic solvent contained equal amounts of Cu and Fe; Fe was then separated by hydroxide precipitation.[21]

Thus, the possibility of using reverse ME in the system SDS–1-butanol–caproic acid–kerosene–water for the selective extraction of non-ferrous metals and their separation from iron already at the leaching stage has been shown. This makes it possible to combine the stages of leaching and liquid extraction when processing raw materials containing non-ferrous metals. The rate of the microemulsion leaching and the recovery of metals from raw materials can be increased, for example, by reducing the particle size of the solid phase, increasing the ultrasonic power, increasing the concentration of the extractant in the ME, or by carrying out leaching in several stages.

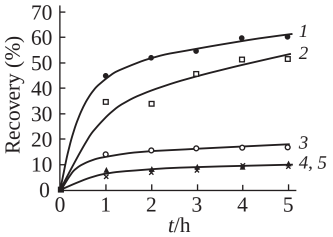

Figure 3 Microemulsion leaching of metals using a sample of oxidized cobalt–copper concentrate: (*1*) Cu, (*2*) Co, (*3*) Mn, (*4*) Fe and (*5*) Ni.

Further, ME can be destroyed by adding an aqueous solution of acid, ions of non-ferrous metals and Na^+ will pass into the aqueous phase, and the organic phase will contain caproic acid, butanol and surfactant in the H-form, making it possible to reuse the organic phase (*cf*. ref. 12). To isolate and purify non-ferrous metals that have passed into the aqueous phase, well-known methods of liquid extraction, ion exchange or electrolysis can be used. Another patented[22] approach describes the leaching of zinc from galvanic sludge into ME and the subsequent precipitation of ZnO nanoparticles under the action of a NaOH solution on this ME.

The results obtained can serve as a basis for the development of energy- and resource-saving processes for hydrometallurgical processing of ore and technogenic raw materials containing non-ferrous metals and iron.

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