# Fractionation of Metal Ions from Water Using Supercritical Carbon Dioxide

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Heavy metals are usually present in the wastewater discharged from electronic and chemical plants, and have been proven to be hazardous to human beings due to their toxicity, bioaccumulation, and carcinogenicity. This pollution problem has become an important issue because many contamination cases involving rice, soil, or groundwater caused by discharged wastewater have been reported. To remove metals from water, several techniques have been developed; however, each one has its inherent limitation. For example, the most widely used method is accomplished by means of direct precipitation (Ku and Peters, 1986), which usually results in contaminated sludge that has to be landfilled; in addition, the sludge later pollutes ground water. Therefore, the development of a more acceptable method is urgently needed.

Recently, supercritical fluid extraction has become a promising alternative for removing organic pollutants when supercritical carbon dioxide (SC $CO_2$) is used as a solvent, due to its desirable properties, including low critical conditions, nontoxicity, nonflammability, and good transport properties. However, chelation with a suitable organic ligand can convert the charged metal species into neutral forms, and the complexes formed are readily soluble in supercritical carbon dioxide (Tait, 1992; Laintz et al., 1992b). Recent reports show that commercially available Cyanex™ 302 (diisooctly-thiophosphinic acid) is an effective ligand for SC $CO_2$ extraction of most metals from a variety of matrices, such as cellulose, sand, clay, wood, and soil (Smart et al., 1997; Kersch et al., 1999), using a small vessel of less than $5\times10^2$ $cm^3$. More recently, Tai et al. (2000) studied the extraction efficiency and kinetics of zinc ion from aqueous solution in a $1.3\times10^3$ $cm^3$ stirred vessel, using the same chelating agent. So far, most of the systems studied contain only one metal; however, the wastewater from streams usually contains a mixture of ions. This motivated us to study the feasibility of developing a separation process for removing and fractionating metal ions from water, using SC $CO_2$ as the solvent, since it usually exhibits a wide range of solubility for different solutes (McHugh and Krukonis, 1994). Some solubility data of ion-chelate complex in SC $CO_2$ are reported in the literature (Laintz et al., 1992a; Smart et al., 1997; Wai and Wang, 1997). These data cannot be applied to this study, because either the operating conditions are different or the chelating agents are not the same.

## Experimental Section

The experimental apparatus is shown in Figure 1. The system consists of three main parts: (I) a feeding system containing a $CO_2$ cylinder, a cooler, and a mini-pump; (II) a pressurized reaction-extraction vessel equipped with a stirrer, a viewing window, a sample valve, and a coil connected to a water bath; and (III) a pressure releasing system with a metering valve, a solid collector, a flow meter, and a gas-bubbling vessel arranged in series. A detailed description of each component has been given elsewhere (Tai et al., 2000; Tai et al., 2001). Here, the experimental procedures are briefly described.

At the beginning of an experiment, $8\times10^2$ $cm^3$ aqueous solution with a desired concentration of a metal salt or a mixture of metal salts was preheated and then fed into the extraction vessel, which was maintained at 315 K. In addition, a 4-$cm^3$ or 8-$cm^3$ amount of Fluka technical grade Cyanex™ 302 was injected into the vessel using a syringe. The amount of this chelating agent was set to be in excess, at least 10 times that of the metal ions on a molar basis according to the following equation

$$\underset{\text{(metal ion)}}{M^{2+}} + \underset{\text{(Cyanex 302)}}{2C_{16}H_{35}OPS} \leftrightarrows \underset{\text{(metal complex)}}{M(C_{16}H_{34}OPS)_2} + 2H^+ \tag{1}$$

The concentration change of the chelating agent in the reaction-extraction process was small, and the concentration effect of

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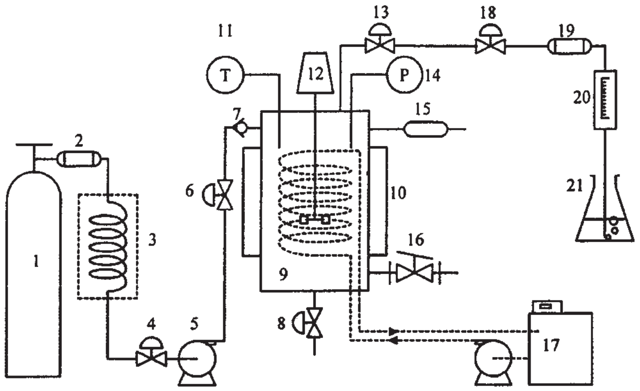

**Figure 1. Experimental apparatus.**

(1) $CO_2$ cylinder; (2) filter; (3) cooler; (4) ball valve; (5) mini-pump; (6) ball valve; (7) check valve; (8) feeding valve; (9) stirred tank; (10) windows; (11) thermometer; (12) agitator; (13) ball valve; (14) pressure gauge; (15) rupture disc; (16) sampling valve; (17) water bath; (18) metering valve; (19) collector; (20) flow meter; (21) water vessel.

Cyanex™ 302 could be assumed to be negligible in the kinetic study.

Then, liquid carbon dioxide was delivered to the unstirred vessel until the pressure reached the desired value, which varied from run to run between 8.3 and 13.8 MPa. At this moment, the amount of Cyanex™ 302 added to the vessel was completely dissolved in SC $CO_2$, as observed through the viewing windows of the extraction vessel. Then the agitator started to operate with a stirring rate varying from 7.2 to 17.7 $s^{-1}$ in different runs. Very soon, SC $CO_2$ droplets were well dispersed in the water solution, and the system pressure and temperature became steady. The liquid solution was then sampled at appropriate intervals, and the samples were analyzed using an inductively coupled plasma (ICP) spectrometer.

## Results and Discussion

### *Removal of single ions*

Several metal ions, including $Cu^{2+}$, $Zn^{2+}$, $Pb^{2+}$, and $Ni^{2+}$, were tested in this study. Experiments were first conducted to investigate the removal of single metal ions, and then systems composed of two and three-ion mixtures were examined for fractionation.

### *Extraction efficiency of single ion system*

The ion concentration usually leveled off after 30 min of operating time. Typical results are shown in Figure 2 for $Zn^{2+}$. Therefore, the extraction efficiency was defined as follows

$$\% \text{ extraction} = \frac{\text{metal ion loaded} - \text{metal ion remaining}}{\text{metal ion loaded}} \times 100\% \quad (2)$$

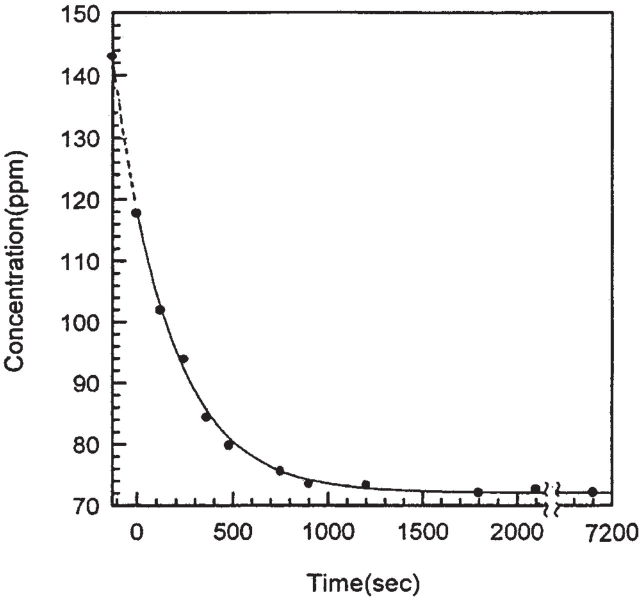

**Figure 2. Concentration profile of $Zn^{2+}$ in aqueous solution.**

Operating conditions: temperature 313 K, pressure 8.3 MPa, stirring rate 13.2 $s^{-1}$, chelating agent 4 $cm^3$.

The extraction efficiencies of different ions under the specified operation conditions are listed in Table 1. For $Cu^{2+}$ and $Pb^{2+}$, extraction was almost complete; for $Zn^{2+}$, an appreciable amount remained for an initial concentration of 202 ppm, and extraction was almost complete for an initial concentration of 55 ppm; for $Ni^{2+}$, extraction was ineffective. It was clear that the extraction efficiency of $Zn^{2+}$ depended on the initial concentration of $Zn^{2+}$. Since the amount of chelating agent was in excess, the extraction efficiency of $Zn^{2+}$ was probably limited by the solubility of the ion-chelate complex in supercritical $CO_2$. However, the formation of $Ni^{2+}$-chelate complex proceeded to a limited extent that caused the low efficiency of $Ni^{2+}$ extraction. Laintz et al. (1998) used acetylacetone instead of Cyanex™ 302 as a chelating agent for the extraction of $Ni^{2+}$.

### *Fractionation of ion mixtures*

The recovery of individual components from waste streams containing a mixture of species is a key step in a practical separation process since waste streams discharged from electronic or chemical plants usually contain more than one ion. It is, therefore, interesting to study the feasibility for recovering separate ions by varying the operating conditions, using supercritical $CO_2$. Here, the binary system $Cu^{2+}/Zn^{2+}$ was taken as a model system. The separation of $Cu^{2+}$ and $Zn^{2+}$ seemed to depend on the ion concentration, and the amount of chelating agent. As shown in Figure 3, when the concentration levels of

**Table 1. Extraction Efficiency for Different Metal Ions**

| Metal Ion | Initial Concentration (ppm) | Final Concentration (ppm) | % Extraction |
|---|---|---|---|
| $Cu^{2+}$ | 140 | ~0 | ~100 |
| $Pb^{2+}$ | 51 | ~0 | ~100 |
| $Zn^{2+}$ | 55 | 5 | 90.9 |
| $Zn^{2+}$ | 202 | 125 | 61.9 |
| $Ni^{2+}$ | 83 | 80 | 3.6 |

Operating conditions: pressure 8.3–9.1 MPa, temperature 313 K, stirring rate 10.9 $s^{-1}$, Cyanex 302 4 $cm^3$, aqueous solution 0.8 $dm^3$, and reaction time 1,800 seconds.

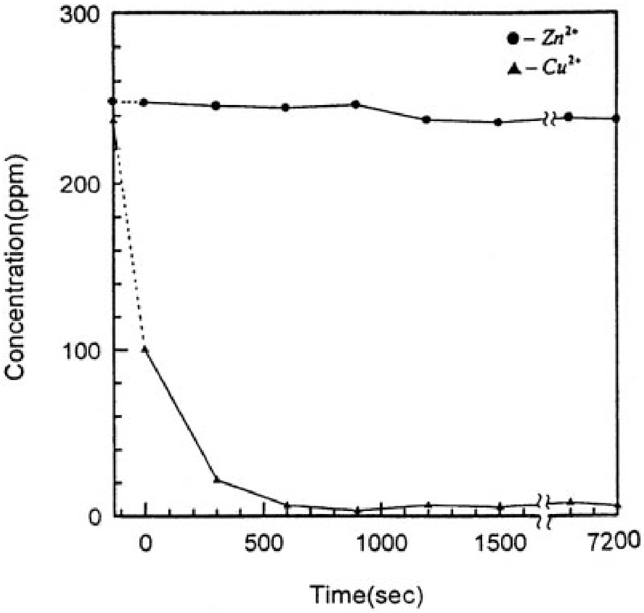

**Figure 3. Concentration profiles of $Zn^{2+}$ and $Cu^{2+}$ extracted from a solution containing both ions.**

Operating conditions: the same as those shown in Figure 2.

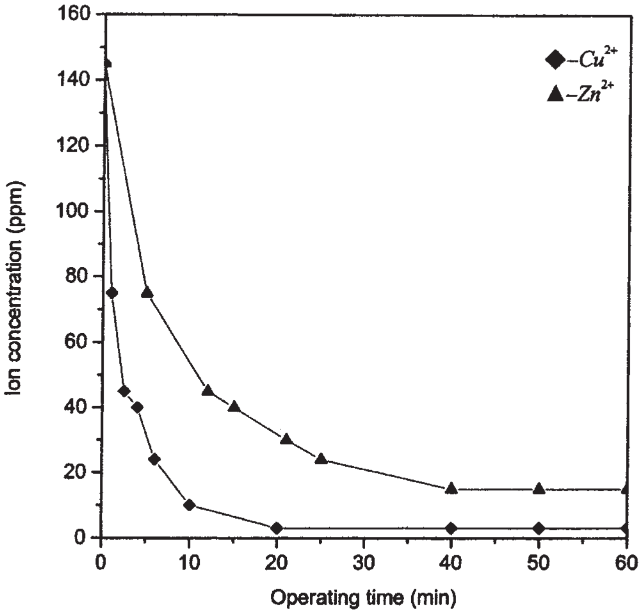

**Figure 5. Concentration profiles of $Zn^{2+}$ and $Cu^{2+}$ extracted from a solution.**

Operating conditions: temperature 313.5 K, pressure 8.3 MPa, stirring rate 10.7 $s^{-1}$, chelating agent 8 $cm^3$.

both ions were at 250 ppm, the extraction of $Cu^{2+}$ was almost complete, but the $Zn^{2+}$concentration remained unchanged when 4mL Cyanex 302 was used. When both ions at lower concentrations, that is, $Cu^{2+}$ at 80 ppm, and $Zn^{2+}$ at 47 ppm, were extracted using the same amount of Cyanex, $Cu^{2+}$ was removed first, and the extraction of $Zn^{2+}$ was not efficient until $Cu^{2+}$ was essentially removed as shown in Figure 4. In this case, the recovery of individual species was possible. However, when the aqueous solution of $Cu^{2+}$ and $Zn^{2+}$ at a concentration of 145 ppm was extracted using 8 mL Cyanex™ 302, both ions were extracted simultaneously as shown in Figure 5. When the aqueous solution contained $Cu^{2+}$, $Zn^{2+}$, and $Ni^{2+}$, the recovery of individual ions was possible as shown in Figure 6, which shows that the removal of $Cu^{2+}$ was complete at 350 s, after which, the concentration of $Zn^{2+}$ started to fall, and the con-

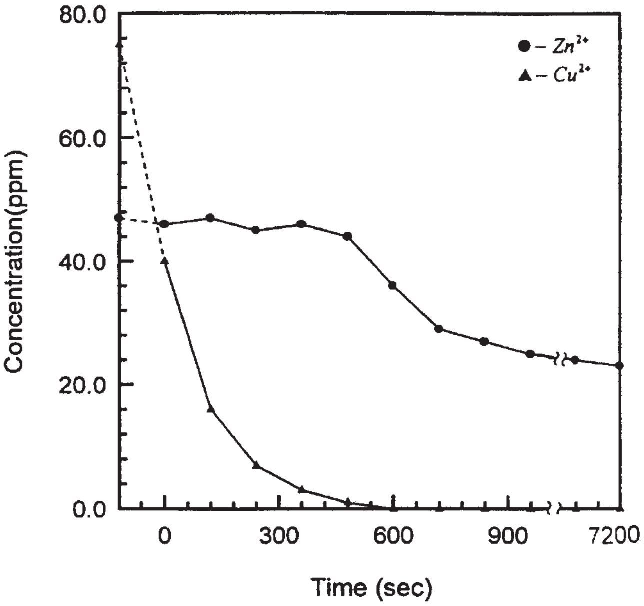

**Figure 4. Concentration profiles of $Zn^{2+}$ and $Cu^{2+}$ extracted from a solution containing both ions of a lower level.**

Operating conditions: the same as those shown in Figure 2.

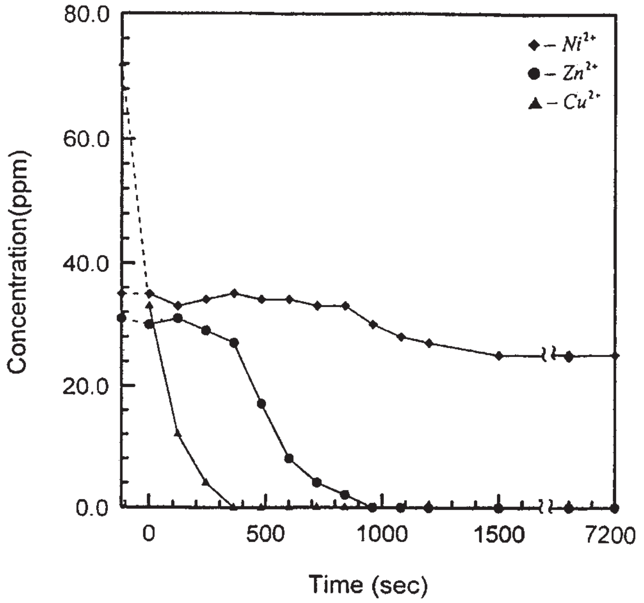

**Figure 6. Concentration profiles of $Zn^{2+}$, $Cu^{2+}$, and $Ni^{2+}$ extracted from a solution.**

Operating conditions: temperature 313 K, pressure 8.3 MPa, stirring rate 13.2 $s^{-1}$, chelating agent 8 $cm^3$.

centration of $Ni^{2+}$ remained essentially unchanged for a long operating period. The removal of $Ni^{2+}$ could be achieved using acetylacetone instead of Cyanex 302, as suggested by Laintz et al. (1998).

The mechanism of this extraction process is rather complicated. Mass-transfer takes place between phases in a stirred tank, in which coarse droplets of SC $CO_2$ in water are formed as SC $CO_2$ disperses into the aqueous solution. Then metal ions are transported to the $H_2O$/SC $CO_2$ interface, and react with the chelating agent to form a complex, which is soluble in SC $CO_2$. The extraction efficiency of individual ions depends on the equilibrium constant between the ion and ion-chelate complex as indicated by Eq.1, and on the solubility of the ion-chelate complex in SC $CO_2$. Thus, the extraction of $Ni^{2+}$ is limited either by a low equilibrium constant or low solubility of the complex. The competing behavior between $Cu^{2+}$ and $Zn^{2+}$ is determined by the reaction rate of complex formation, or by the diffusion rates of the ion in aqueous phase, and the ion-chelate complex in SC $CO_2$ phase. The related equilibrium data and rate data are not available at this time. Much work needs to be done to collect all the data needed for the prediction of a working system of an ion mixture. This work is currently underway in our laboratory.

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