

Extraction of Heavy Metals from Fly Ash and Sand with Ligands and Supercritical Carbon Dioxide

C. Kersch,* M. J. E. van Roosmalen, G. F. Woerlee, and G. J. Witkamp

Laboratory for Process Equipment, Delft University of Technology,
Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

This project further develops supercritical fluid extraction as an industrial remediation process for soil and other heavy-metal-contaminated solid materials. In this study, divalent metals such as Zn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , and Cr^{3+} are removed from sand and fly ash using CO_2 . When the solvating power of supercritical CO_2 is combined with the metal ion complexing power and selectivity of organic ligands, a clean alternative to conventional liquid–liquid and liquid–solid extraction is obtained. Extraction technologies are required, which not only remove the mobile or total fraction of metals but also maintain the matrix's morphology and structure. In particular, the reuse of fly ash as construction or landfill material becomes possible with the application of supercritical fluid technology. In a study with spiked sand samples, the effect of pressure, the humidity of the contaminated material, and the use of methanol as the entrainer in CO_2 on the extraction efficiency is investigated. Influences of the type of complexing ligands is studied with both fly ash and sand samples. It is shown that the use of methanol as the entrainer and the humidity have strong effects on the metal extraction.

Introduction

Leaching procedures are known to remove heavy metals from soil, sludge, or compost at atmospheric pressure. This often requires a large amount of solvents, which must afterward be treated with neutralizers and disposed of. This is of both economic and environmental concern.

Supercritical fluid extraction (SFE) with CO_2 has become a promising alternative to conventional solvent extraction for the cleaning of environmental samples. Compared with conventional solvent extraction, SFE is relatively fast and its selectivity can be controlled. When combined with an appropriate complexing agent, supercritical (SC) CO_2 is a strong solvent with a high diffusivity and a low viscosity. Furthermore, because it can be recycled easily, the absence of solvent waste is a major advantage.

Most of the studies so far have concentrated on the extraction of CO_2 -soluble hydrocarbons from contaminated mixtures. In order for heavy metals to be dissolved in CO_2 , the metals must be present as electrically neutral complexes. Therefore, organic ligands are added to form metal complexes. This effect was first used in the supercritical chromatography of metal complexes by Bickmann and Wenclawiak.¹ In addition, Laintz and Wai² calculated the solubility of metal complexes in studies on the separation of heavy metals from solids by SC CO_2 containing organic ligands. This technology has been extended to contaminated soil and sludge by the group of Wai^{3–6} and Ashraffkhorassani.⁷ To date, all studies have focused on extraction from relatively small (0.1–1 g) aqueous and sludge samples, using a single batch extraction.

This study aims to develop a technical process to remove heavy metals from fly ash and sludge samples of up to 10 L. In this study, extraction from coal fly ash

and spiked sand has been carried out. The extraction efficiency possible with different ligands is studied, along with the influence of pressure, water concentration, and an entrainer.

Materials and Methods

Ligands. The selection of ligands is a key parameter in determining the effectiveness of the extraction process and greatly influences the costs of metal removal. Many complexing ligands have been developed over the last years. Most of the ligands are used for solvent extraction with organic solvents at ambient pressure and only a few of them for SFE. Ligands may be characterized in terms of four classes, which are based on the type of reaction that occurs between the metal and the ligand. These classes are (1) acid ligands, (2) acid chelating ligands, (3) anion exchangers, and (4) solvating ligands.

A suitable ligand for SFE shows a high complexation with heavy metals and is highly soluble in SC CO_2 . Ideally the ligand is also selective for specific metals and is easy to recycle. The complexing agents used in conventional solvent extraction processes can also be used in SFE complexation of metal ions, provided they are soluble in SC CO_2 . A variety, but insufficient number, of ligand solubilities have been tested for the SFE of metals.

The extraction of metals usually involves one of two possible aims. First, high extraction efficiencies of all metals are desired for the cleaning of, for example, fly ash or contaminated ground. For other applications (e.g., separation of metals from a mixture of metals), a highly selective extractant would be desired. Ideally, one or more desired elements are extracted reasonably well while few of the undesired elements are extracted from the material which they are faced with.

In this work, SFE is carried out using the acid ligands Cyanex 302 [bis(2,4,4-trimethylpentyl)monothiophosphinic acid], D_2 EHPA [bis(2-ethylhexyl)phosphoric acid], D_2 EHTPA [Bis(2-ethylhexyl)monothiophosphoric acid],

* To whom correspondence should be addressed. E-mail: christof@mail.api.tudelft.nl. Phone: +31 15 278 3839. Fax: +31 15 278 6975.

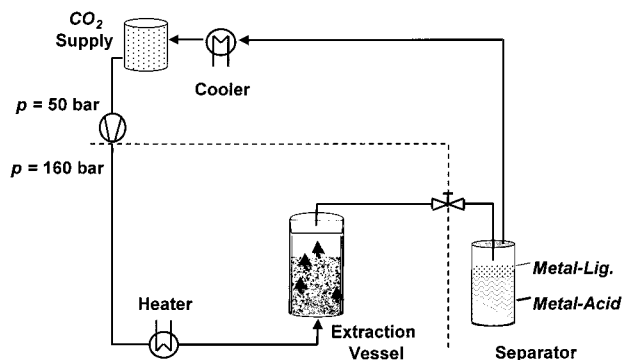


Figure 1. Extraction process and the CO₂ cycle.

DiOPA (diisooctylphosphinic acid), the acid chelating ligand NaDDC (sodium diethyldithiocarbamate), the anion-exchanger Aliquat 336 (methyltriocylammonium chloride), and the solvating ligand Cyanex 923, a mixture of tertiary octyl- and hexylphosphine oxides.

Apparatus and Experimental Section

Prior to the extraction experiments with spiked sand, the samples were prepared by loading dry sand (SiO₂, 0–1 mm) with stock solutions of zinc (Zn²⁺), copper (Cu²⁺), lead (Pb²⁺), cadmium (Cd²⁺), and chromium (Cr³⁺). In each case the resulting concentration of Zn²⁺ was ~250 ppm and the individual concentration of all other ions ~50 ppm. The samples were dried for 2–3 h at 65 °C. Fly ash samples were prewetted to a total water content of 10 wt %.

Carbon dioxide was supplied from a supply tank, maintained at a pressure of approximately 50 bar (see Figure 1). The tank was filled with liquid CO₂ from the recycle stream and fresh carbon dioxide from storage. CO₂ was pressurized and passed through a heat exchanger before it entered the preheated 400 mL extraction vessel. After the extraction vessel, the pressure of the carbon dioxide stream was reduced to 50 bar via a pressure control valve. This extract was fed into a 17 L separator containing 3 L of 3 M nitric acid to collect the metal–ligand complex. The expanded neat carbon dioxide was evaporated from the separator, condensed in a heat exchanger, and then returned to the carbon dioxide supply vessel.

After mixing 20 g of spiked sand with 2 mL of pure ligand or 100 g of fly ash with 5 mL of ligand, the mixture was placed in the preheated extraction vessel. For Aliquat 336 experiments, 3 mL of a 3.3 M NaCl solution was added to the mixture.

Subsequently, the vessel was pressurized with SC CO₂. The time of dynamic extraction for sand was 40 min when using a flow rate of ~3 kg of CO₂/h. Halfway through the sand experiments, an additional 1 mL of ligand was fed to the autoclave. Fly ash was statically extracted for 10 min, followed by 30 min of dynamic extraction using a flow rate of ~3 kg of CO₂/h.

When the extraction was completed, the sand/fly ash was removed from the extraction vessel. The sand was treated with 1 M HNO₃ at a temperature of 50 °C. The fly ash was digested for 20 min in a microwave with HF (40%) and HNO₃ (65%) at a temperature of 180 °C. The subsequent solutions were analyzed with a high-resolution ICP-MS (induction coupled plasma mass spectroscopy). The treated sand sample and fly ash sample were respectively compared with unprocessed matrixes and nonloaded samples. The extraction ef-

Table 1. Ligand Influence on the Extraction Efficiency [%] from Dry Sand ($p = 160$ bar, $T = 45$ °C, $t_{\text{extr}} = 40$ min)

	Cyanex 302	Aliquat 336	D ₂ EHPA	DiOPA	CO ₂	reproducibility [%]
Pb	11	6	1	<1	<1	3
Zn	50	7	41	62	<1	2
Cd	41	40	2	<1	4	5
Cu	46	<1	12	13	3	5
Hg	99	98	96	86	34	6

Table 2. Pressure Influence on the Extraction Efficiency [%] from Dry Sand, Using Cyanex 302 ($p = 160$ bar, $T = 45$ °C, $t_{\text{extr}} = 40$ min)

	80 bar	120 bar	160 bar	200 bar	reproducibility [%]
Pb	2	6	11	21	3
Zn	5	28	50	55	2
Cd	6	21	41	49	5
Cu	8	29	46	55	5

iciency was defined as

$$\% \text{ extraction} = \left(1 - \frac{\text{metal on treated spiked sand or fly ash [ppm]}}{\text{metal on untreated spiked sand or fly ash [ppm]}} \right) \times 100\% \quad (1)$$

Each experiment is performed three times. The maximum deviation of the analysis from the average is defined as reproducibility.

In addition to the influence of different ligands, the effect of variables such as pressure, entrainer, and matrix humidity on the extraction efficiency from fly ash and spiked sand was studied.

Results: Spiked Sand

Ligands. The first series of experiments was carried out to establish the influence of the ligands. In these experiments, Cyanex 302, Aliquat 336, DiOPA, and D₂-EHPA were tested. Table 1 shows the results obtained from experiments at 160 bar and 45 °C. A negligible amount of metals were extracted when no ligands were used. The high extraction efficiency of Hg²⁺ probably originates from the high volatility of Hg²⁺. Cyanex 302 was better able to extract Zn²⁺, Cd²⁺, and Cu²⁺ rather than Pb²⁺. Aliquat 336 shows poor extraction efficiencies, with the exception of Cd²⁺. With D₂EHPA or DiOPA, the extraction efficiency of Zn²⁺ was moderate, while small amounts of Cu²⁺ and almost no Pb²⁺ and Cd²⁺ were extracted.

Density (with Pressure at a Given Temperature). The density influence on extraction was investigated at a given temperature by increasing the pressure. The results are shown in Table 2. Increased pressure, and thus density, enhances the extraction efficiency of most of the metal ions from less than 10% to about 50%. The extraction efficiency of Pb²⁺ was raised from 2% to 21% at 80 and 200 bar, respectively.

Water. One aim of this study is to remove heavy metals from sludges, e.g., river and harbor sludges. An important parameter for sludge treatment is the water concentration in the matrix. The water content in the sample was defined as

$$\% \text{ water} = \left(\frac{\text{water [g]}}{\text{water} + \text{dry matrix [g]}} \right) \times 100\% \quad (2)$$

Prior to extraction, ultrapure water was added to vary the humidity. The results are shown in Table 3. For all metals, a maximum efficiency is obtained for water

Table 3. Influence of Water Content (wt %) on the Extraction Efficiency [%] from Spiked Sand, Using Cyanex 302 ($p = 160$ bar, $T = 45$ °C, $t_{\text{extr}} = 40$ min)

	0	5	10	15	25	reproducibility [%]
Pb	11	64	69	68	27	3
Zn	50	79	76	69	48	2
Cd	41	95	>99	98	48	5
Cu	46	99	99	98	51	5

Table 4. Influence of Entrainer (5 wt % Methanol in CO₂) on the Extraction Efficiency [%] from 20 g of Dry Sand, Using Cyanex 302 ($p = 160$ bar, $T = 45$ °C, $t_{\text{extr}} = 40$ min)

	CO ₂	CO ₂ + methanol	reproducibility [%]
Pb	11	87	3
Cd	41	99	5
Cu	46	99	5
Cr	<1	52	5

Table 5. Influence of Ligand on the Extraction Efficiency [%] from Fly Ash (10 wt % Humidity, $p = 160$ bar, $T = 45$ °C, $t = 10/30$ min)

	Cyanex 302	D ₂ EHTPA	NaDDC	Cyanex 923	reproducibility [%]
Cr	10	17	9	9	5
Sb	9	12	1	4	6
V	6	13	6	5	5
Mo	12	18	5	9	5

concentrations between 5 and 10 wt %. The most significant rise in efficiency was noted for Pb²⁺. At 10 wt % sand moisture, Cd²⁺ and Cu²⁺ are extracted almost completely. The efficiency of Zn²⁺ is maximal at 5 wt % and decreases linearly with increasing humidity.

Entrainer. To enhance the extraction efficiency, the use of an entrainer was investigated. Methanol addition modifies the polarity of the CO₂ phase and favors the mobility of metal chelates. A higher extraction efficiency of Hg²⁺ (from spiked filter paper and 0.3 g of spiked sand samples) has been obtained previously⁵ using proton-ionizable crown ethers and methanol-modified CO₂.

Table 4 shows the influence of methanol-modified CO₂ on the extraction from spiked sand containing the phosphinic acid Cyanex 302. Methanol was sprayed continuously into CO₂ before the inlet of the extraction vessel to maintain a concentration of 5 wt %. The efficiencies with neat CO₂ vary from about 43% of Cd²⁺ and Cu²⁺, to poor extraction of Pb²⁺, and almost no extraction of Cr³⁺. When methanol is added, half of the Cr³⁺ is extracted. Cd²⁺ and Cu²⁺ are extracted almost entirely (99%), and the efficiency of Pb²⁺ increases to about 90%.

Results: Fly Ash

Because high extraction efficiencies from spiked sand are observed, extraction from fly ash from a coal-fired power plant was studied. The aim is the extraction of leachable heavy metals by SFE. Table 5 shows the results using different ligands. All metals are extracted best from fly ash using D₂EHTPA. Cyanex 302 results in slightly less extraction. The average extraction efficiency is around 10%. The extraction efficiency refers to the total amount of metals in the fly ash. Because most of the metals of a fly ash particle are bound in the glass matrix of the particle's core, only a relatively small amount of metals are leachable. The low extraction efficiencies in Table 5 imply that only the leachable metals are extractable by SC CO₂.

Discussion and Conclusion

The extraction efficiency of heavy metals from sand matrixes with SC CO₂ is influenced by a number of process parameters. Because of the sample preparation, the spiked metals are on the surface of the sand crystals. It must be taken into account that in most natural samples the particle morphology is influencing the mass transport. The experiments carried out in this study show that addition of a complexing ligand is necessary to extract metals. Experiments with pure CO₂ result in no (1–2%) extraction of metals. The experiments indicate that Cyanex 302 results in efficiencies of greater than 50% for most of the metals. The amount of Cd²⁺ extracted with Aliquat 336, in combination with a NaCl solution, was significantly greater than that for all other metals tested. D₂EHTPA and DiOPA are most effective for the extraction of Zn²⁺. In general Hg²⁺ was removed from the matrixes entirely. Extraction temperatures of 45 °C, coupled with a high volatility of Hg²⁺, are probably the cause of this effect. It was shown that higher pressures enhance the complex solubility in CO₂, leading to more effective extraction. The extraction was significantly affected by the water content of the matrix. This study showed that the highest extraction efficiencies are obtained at water concentrations in the range of 5–10 wt %. Under these conditions an extraction efficiency of 99% was obtained for Cd²⁺ and Cu²⁺. Almost complete extraction of Cd²⁺ and Cu²⁺ was achieved using methanol-modified (7 mol %) CO₂. Using Cyanex 302, the extraction of Cr³⁺ was only possible with methanol-modified CO₂.

SFE from fly ash can, in general, be used to reduce the leachable metals of the fly ash particle. Leachability tests after SFE will show a more detailed impact of SFE on the reduction of metals from fly ash. It has been demonstrated that SFE can be used for the extraction of divalent metal ions from either spiked sand or fly ash.

Acknowledgment

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Literature Cited

- (1) Bickmann, F.; Wenclawiak, B. Supercritical fluid chromatography of various metal chelates of 8-hydroxyquinoline, diethyldithiocarbamate and acetylacetone. *Fresenius' Z. Anal. Chem.* **1985**, 320 (3), 261.
- (2) Laintz, K. E.; Wai, C. M. Solubility of Fluorinated Metal Diethyldithiocarbamates in Supercritical Carbon Dioxide. *J. Supercrit. Fluids* **1991**, 4, 194.
- (3) Lin, Y.; Wai, C. M. Supercritical Fluid Extraction of Lanthanides With Fluorinated β -Diketones and Tributyl Phosphate. *Anal. Chem.* **1994**, 66, 1971.
- (4) Wai, C. M. Supercritical Fluid Extraction of Lanthanides and Actinides With Fluorinated β -Diketones. *Proc. 3rd Int. Symp. Supercrit. Fluid, Strasbourg* **1994**, 2, 31.
- (5) Wang, S.; Elshani, S.; Wai, C. M. Selective Extraction of Mercury With Ionizable Crown Ethers in Supercritical Carbon Dioxide. *Anal. Chem.* **1995**, 67, 919.
- (6) Smart, N. G.; Carleson, T. E.; Elshani, S.; Wang, S.; Wai, C. M. Extraction of Toxic Heavy Metals Using Supercritical Fluid Carbon Dioxide Containing Organophosphorus Reagents. *Ind. Eng. Chem. Res.* **1997**, 36, 1819.
- (7) Ashrafkhorassani, M. Supercritical Fluid Extraction of Mercury Ion and Mercury Complexes From Different Matrixes. *Proc. 3rd Int. Meeting Supercrit. Fluid, Nice* **1998**, 749.

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