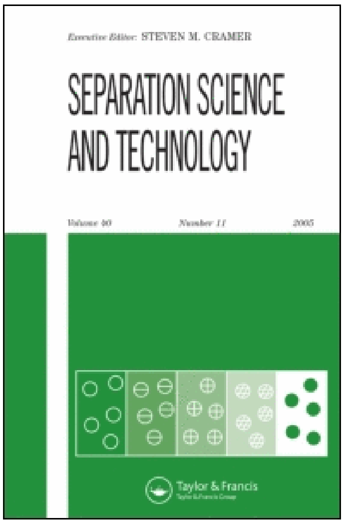

Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Chlorination Separation of Uranium, Thorium, and Radium from Low-Grade Ores

V. S. Sastri[a]; J. R. Perumareddi[b]
[a] METALS TECHNOLOGY LABORATORIES CANMET, ONTARIO, CANADA [b] DEPARTMENT OF CHEMISTRY, FLORIDA ATLANTIC UNIVERSITY, BOCA RATON, FLORIDA, USA

To cite this Article Sastri, V. S. and Perumareddi, J. R.(1995) 'Chlorination Separation of Uranium, Thorium, and Radium from Low-Grade Ores', Separation Science and Technology, 30: 1, 153 — 158
To link to this Article: DOI: 10.1080/01496399508012220
URL: http://dx.doi.org/10.1080/01496399508012220

SEPARATION SCIENCE AND TECHNOLOGY, **30**(1), pp. 153–158, 1995

TECHNICAL NOTE

Chlorination Separation of Uranium, Thorium, and Radium from Low-Grade Ores

---

V. S. SASTRI
METALS TECHNOLOGY LABORATORIES
CANMET
568 BOOTH STREET, OTTAWA, ONTARIO, K1A 0G1, CANADA

J. R. PERUMAREDDI
DEPARTMENT OF CHEMISTRY
FLORIDA ATLANTIC UNIVERSITY
BOCA RATON, FLORIDA, USA

ABSTRACT

Low-temperature chlorination of low-grade uranium ores containing uranium in the 0.02 to 0.06% range, thorium in the 0.036 to 0.12% range, and radium in the 70 to 200 pci/g range resulted in the extraction of >90% of the constituents. The residue left after chlorination was found to be innocuous and suitable for disposal as a waste acceptable to the environment. Use of sodium chloride in the charge was useful in reducing the chlorination temperature and in the formation of nonvolatile anionic chloro complexes of the metal ions in the ore.

INTRODUCTION

Increasing depletion of high-grade uranium ores and increased concern for the safe disposal of radioactive solid wastes have resulted in the demand for new processes for the efficient extraction of uranium, thorium, and radium from low-grade uranium ores.

The current commercial extraction process (1) involves leaching of the uranium ore with sulfuric acid followed by ion-exchange separation of anionic uranyl sulfate complex from the leach liquor and subsequent precipitation of uranium as the diuranate, also known as the yellow cake (80–85% U_3O_8). Environmental concerns associated with this process are generation of sulfuric acid within the tailings caused by the slow oxidation of pyrite:

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4$$

$$2FeSO_4 + \frac{1}{2}O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$$

and the subsequent solubilization of metal ions such as Cu, Zn, Pb, Ti, Co, Ni, Th, and Mo, and radionuclides such as ^{235}U, ^{230}Th, ^{226}Ra, and ^{210}Pb. These metal ions and radionuclides cause environmental problems in the biosphere.

Improvements to the current uranium extraction process and development of new processes for the extraction of uranium may alleviate the problems of environmental concern. Two requirements of the new process are: efficient extraction of ^{226}Ra, and the production of tailings low in pyrite that would be suitable for further disposal.

The development of a new process to remove ^{226}Ra, which forms sparingly soluble sulfate, requires a total departure from conventional sulfuric acid leaching. Sulfate ions originating from acid addition or the oxidation of pyrite hinders the recovery of ^{226}Ra.

This paper deals with bench-scale studies directed toward the development of a new process for the extraction of uranium by low-temperature chlorination in the presence of sodium chloride. Radium and thorium are also extracted with uranium, leaving an innocuous residue with a reduced pyrite content.

EXPERIMENTAL

The chlorination apparatus consisted of a 100-cm-long by 6-cm-i.d. fused silica reaction tube heated in a 75-cm-long by 7.6-cm-i.d. Lindberg furnace in which the hot zone could be maintained at 500 ± 3°C. A three-way stopcock at the entry side of the silica tube allowed the passage of either nitrogen or chlorine through the tube. Chlorine was passed through a magnesium perchlorate drying tube and a flowmeter before entering the silica tube. A known amount of ore mixed with sodium chloride and charcoal powder in the form of a briquet was placed in a silica boat and placed in the middle section of the silica tube. The exit side of the silica tube was connected to a glass condenser which was connected to a container containing 25% sodium hydroxide solution for the removal of excess unreacted chlorine (2).

All the experiments were conducted on a mixture of 10 g ore (−200 mesh) mixed with 2 g sodium chloride and 1 g charcoal powder. The temperature of the furnace was measured with a calibrated thermocouple.

The charge was heated to 400°C in a current of dry nitrogen for 30 minutes to drive off moisture, and the temperature was increased to 500°C before the introduction of dry chlorine. Chlorination was carried out for 2 hours. At the end of this time, the passage of chlorine was stopped and the charge was allowed to cool in an atmosphere of nitrogen. The charge in the boat was dissolved in 0.1 M HCl at 80°C and filtered. The residue was analyzed for uranium, thorium, and ^{226}Ra.

Uranium and thorium in the calcined residue were determined by x-ray fluorescence spectrometry. Radium-226 in the sample was analyzed as follows (3): Transfer an aliquot of the solution containing ^{226}Ra, add 5 mL concentrated HCl and 200 mL distilled water, and boil for 5 minutes. Add 5 mL of 1 M citric acid solution to the hot solution and then adjust the pH to 8–9 with ammonium hydroxide solution. Add 40 mg lead and 0.5 mg barium nitrate solution to the ammoniacal solution. Place the beaker on a magnetic stirring plate, insert the magnetic stirring bar, add 0.5 g ammonium sulfate solution, and adjust the pH to 1.0 with 1 : 1 sulfuric acid. Stir the solution for 30 minutes. Filter the combined sulfate precipitate of lead, barium, and radium on millipore HABP04700, wash the precipitate with 1% sulfuric acid, and discard the filtrate. Transfer the millipore filter into the original beaker, wash the precipitate with a fine jet of water, then adjust the pH to 8–9 with ammonium hydroxide; add 5 mL of 0.25 M EDTA solution. Rinse the filter with water, discard the filter, and boil the solution. Place the beaker on a magnetic stirring plate, add 0.5 g ammonium sulfate in the form of a solution, and, while stirring, add glacial acetic acid and adjust the pH to 4.0 using a pH meter. Continue stirring for 30 minutes. Filter the precipitate of barium and radium sulfates on a millipore HABP02500 filter disk and discard the filtrate. Dry the filter and mount it on a circle of gummed label and determine ^{226}Ra by alpha spectrometry.

RESULTS AND DISCUSSION

Initial experiments were carried out to determine the optimum conditions such as the reaction temperature, ore-to-carbon ratio, and ore-to-salt ratio.

At 450°C about 95% of the ore reacted with chlorine, and variation of the temperature in the 450 to 600°C range showed little difference in the degree of chlorination of the ore. The extent of chlorination of the ore was determined from the amount of residue left after treatment of the chlorinated charge with 0.1 M hydrochloric acid to solubilize the nonvolatile metal chlorides. At 450 and 500°C, uranium was present both in the volatile and nonvolatile fractions as determined by qualitative tests. At temperatures of 550 and 600°C, the uranium was present in the nonvolatile fraction only.

Chlorination of the ore at 550°C at different ratios of carbon to ore (0:10, 1:10, 2:10, 3:10, 4:10, and 5:10) gave 0, 98, 97, 96, 95 and 94% of reaction, respectively. From these data the ratio of 1:10 of carbon to ore was chosen for further experiments.

The effect of varying the amount of sodium chloride in the charge containing the ore and carbon in the ratio of 10:1 on the chlorination of the ore at 550°C was studied by the addition of sodium chloride in the 1 to 5 g range. At a sodium chloride content of 2 g and above, 99.5% of the uranium was found in the calcine, and it appears from this that the optimum ratio of ore:carbon:sodium chloride is 10:1:2. Sodium chloride in amounts greater than 2 g in the charge adversely affected the extent of chlorination reaction.

Henderson and coworkers (5) as well as Mathur et al. (2) observed that the use of sodium chloride in the charge lowered the reaction temperature along with an acceptable chlorine efficiency. Keeping the optimum ratio of ore:carbon:sodium chloride at 10:1:2, the temperature of the chlorination was varied from 450 to 550°C. The flow rate of chlorine was 3.5 L/h. At 500°C, uranium >99% was found in the nonvolatile fraction, i.e., the calcine. These preliminary experiments showed the optimum conditions for chlorination to be a 10:1:2 ratio of ore:carbon:sodium chloride and a temperature of 500°C at a flow rate of 3.5 L/h of chlorine.

The optimum conditions determined from preliminary chlorination experiments such as a ore:carbon:salt ratio of 10:1:2, a temperature of 500°C, and a flow rate of 3.5 L/h of chlorine were used in the chlorination of three low-grade uranium ores containing thorium and radium; the results are presented in Table 1. Ores of three different compositions were studied. The initial uranium, thorium, and radium contents of the first ore were 0.051 wt%, 0.120 wt%, and 85 pci/g, respectively. The residue of this ore after chlorination and leaching the soluble chlorides analyzed 0.0012 and 0.015 wt% of uranium and thorium, respectively, along with 8 pci/g of radium. In the case of two other ores with uranium contents of 0.022 and 0.062 wt%, chlorination resulted in 91 and 95% extractions, respectively. Corresponding extractions of thorium were 90 and 83%, along with 93 and 89% extractions of radium.

Following the promising results obtained with 10 g of the ore, larger-scale laboratory experiments using 100 g of the ore mixed with 10 g carbon and 20 g sodium chloride were conducted for 2–3 hours; the results showed >90% extraction of uranium, thorium, and radium as soluble chlorides, leaving a residue which is innocuous from the environmental point of view.

TABLE I
Data on the Separation of Uranium, Thorium, and Radium from Ores

		Concentration (wt%)		
		Initial	After chlorination	Extraction (%)
1.	Uranium	0.051	0.0012	97.6
	Thorium	0.120	0.015	92.5
	^{226}Ra	85 pci/g	8 pci/g	91.6
2.	Uranium	0.022	<0.002	>91.0
	Thorium	0.060	0.006	90.0
	^{226}Ra	200 pci/g	14 pci/g	93.0
3.	Uranium	0.062	0.0027	95.6
	Thorium	0.036	0.0062	82.8
	^{226}Ra	70 pci/g	8 pci/g	88.6

The oxides in the ore were converted to chlorides by chlorination in the presence of carbon (4):

$$3\text{MeO} + 2\text{C} + 3\text{Cl}_2 \rightarrow 3\text{MeCl}_2 + \text{CO} + \text{CO}_2$$

Addition of sodium chloride to the charge helped in reducing the chlorination temperature as well as in the formation of nonvolatile anionic chloro complexes of metal ions in the ore (5).

CONCLUSION

Chlorination of low-grade uranium ores containing uranium in 0.02 to 0.06 wt% range, thorium in the 0.036 to 0.120 range, and radium in the 70 to 200 pci/g range using a ore:carbon:salt ratio of 10:1:2 resulted in >90% extraction of the constituents. Sodium chloride in the charge lowered the chlorination temperature and aided the formation of nonvolatile chloro complexes. The residue left after chlorination and solubilization of the metal chlorides was found to be suitable for safe disposal as a waste. Since the solid residue after chlorination contained less than 15 pci/g of ^{226}Ra, it can be used for landfill purposes.

The soluble chlorides of U, Th, and ^{226}Ra is solution could be adsorbed onto an ion-exchange resin and thus effect their recovery, leaving behind an effluent essentially barren in U, Th, and ^{226}Ra ions.

REFERENCES

1. R. C. Merritt, *The Extractive Metallurgy of Uranium*, Colorado School of Mines Research Institute, 1971, Chapters 2 and 5.
2. B. S. Mathur, V. S. Sastri, and Y. W. Gokhale, *J. Sci. Ind. Res.*, *21D*, 5 (1962).
3. K. S. Subramanian and V. S. Sastri, *Sep. Sci. Technol. 15*, 145 (1980).
4. W. J. Kroll, *Met. Ind. (London)*, *81*, 243 (1952).
5. A. W. Henderson, S. L. May, and K. B. Higbie, *Ind. Eng. Chem.*, *50*, 611 (1958).

Received by editor November 16, 1993
Revised May 9, 1994