SEPARATION PROCESSES

Heavy Metals, Ions and Minerals

Edited by

M. Misra

SEPARATION PROCESSES

Heavy Metals, Ions and Minerals

Proceedings of a Symposium sponsored
by EPD Aqueous Processing Committee,
EPD Precious Metals Committee, and jointly
by EPD/LMD Recycling Committee,
held at the TMS Annual Meeting in Las Vegas, Nevada
February 12-16, 1995

江苏工业学院图书馆
藏书章

Edited by
Manoranjan Misra
University of Nevada, Reno
Reno, Nevada

A Publication of
TMS
Minerals • Metals • Materials

A Publication of The Minerals, Metals & Materials Society
420 Commonwealth Drive
Warrendale, Pennsylvania 15086
(412) 776-9000

The Minerals, Metals & Materials Society is not responsible for statements or opinions and is absolved of liability due to misuse of information contained in this publication.

Printed in the United States of America
Library of Congress Catalog Number 94-73536
ISBN Number 0-87339-279-5

Authorization to photocopy items for internal or personal use, or the internal or personal use of specific clients, is granted by The Minerals, Metals & Materials Society for users registered with the Copyright Clearance Center (CCC) Transactional Reporting Service, provided that the base fee of $3.00 per copy is paid directly to Copyright Clearance Center, 27 Congress Street, Salem, Massachusetts 01970. For those organizations that have been granted a photocopy license by Copyright Clearance Center, a separate system of payment has been arranged.

TMS
Minerals • Metals • Materials

© 1995

If you are interested in purchasing a copy of this book, or if you would like to receive the latest TMS publications catalog, please telephone 1-800-759-4867.

Preface

This volume includes the papers presented at the Annual Meeting of TMS in a special symposium on Separation Processes. This Symposium was organized by the Aqueous Processing Committee of the Extractive and Processing Division. EPD extends thanks to all the authors who prepared the manuscripts for this volume and the organizing committee.

Personal thanks to Janel Fontana for handling all the correspondence and to Ashok Raichur for assisting in layouts and assembly. The assistance provided by Janet Urbas of the TMS staff is gratefully acknowledged.

Manoranjan Misra
Editor, Separation Processes Symposium, 1995

Organizing Committee

Manoranjan Misra
University of Nevada, Reno
Reno, Nevada

David Dreisinger
University of British Columbia
Vancouver, British Columbia

Rong-Yu Wan
Newmont Metallurgical Services
Salt Lake City, Utah

此为试读,需要完整PDF请访问: www.ertongbook.com

TABLE OF CONTENTS

Preface v

Removal of Heavy Metals

Recovery of Uranium Using Continuous
Countercurrent Ion Exchange (CCIX™) 3
J. C. Milbourne and I. R. Higgins

Elimination of As, Hg and Zn From Synthetic Solutions
and Industrial Effluents Using Modified Bark 15
I. Gaballah and G. Kilbertus

Selective Separation of Trace Metals
and Organics From Water 27
E. S. Peterson, K. R. Arehart, D. C. Kunerth,
M. L. Stone and R. F. Hammen

Removal of Heavy Metal Ions From Acid Mine Water
by Ferrite Coprecipitation Process 37
K. Yang, M. Misra and R. K. Mehta

Sorption of Copper Ions From Aqueous Solutions
by *Potamogeton Luscens* Biomass 49
I. A. H. Schneider, M. L. de Souza and J. Rubio

Photolysis For Cyanide and Nitrate Remediation of Water 61
C. A. Young, S. P. Cashin, and F. E. Diebold

Biosorption of Heavy Metals and Uranium From Dilute Solutions 81
I. A. H. Schneider, M. Misra and R. W. Smith

Physical Separation of Heavy Metals

Selective Flotation For The Removal of Radionuclides From Contaminated Soil 93
J. D. Miller, Q. Yu and Y. Q. Lu

Flotation Separation of Uranium From Contaminated Soils 111
M. Misra, R. K. Mehta, H. Garcia, C. D. Chai and R. W. Smith

Loading and Froth Flotation of a Chelating Ion-Exchange Resin 123
S. Duyvesteyn and F. M. Doyle

The Mineral Graphite Purification in Reactive Froth 135
F. K. Letowski

The Role of Physical Separation Processes in a Proposed Physicochemical Soil Washing System at Fernald 149
M. A. Krstich and R. J. Gibson

Air Separation of Heavy Metal Contaminants from Soil 157
M. E. Nelson, M. J. Harper and A. D. Buckon

Phosphate Beneficiation - Challenges and Opportunities 167
J. Zhang

Hydrometallurgical Separations

Gold Recovery From Organic Solvents Using Galvanic Stripping 187
C. Flores and T. J. O'Keefe

Germanium - An Aqueous Processing Review 203
R. J. M. van Lier and D. B. Dreisinger

Impurity Levels in Hematite Produced by Autoclave Hydrolysis of Ferric Nitrate 225
G. Van Weert and V. Kok

Oxidation of Chalcopyrite by 'In-Situ' Electrogenerated
Fe^{III} and Cu^{II} Using An Ion Exchange Membrane 235
S. Ivanaj and I. Gaballah

The Kinetics of The Solubility of Amorphous
Fe(III)-As(V) Precipitates 247
E. Vircikova, L. Molnar and P. Lech

Recovery of Zinc, Copper and Nickel From Industrial Effluents Generated
By The Electroplating Units Using The "3PE" Technology 257
P. Aguirre, I. Gaballah, B. Fenouillet, S. Ivanaj,
G. Lacoste and R. Solozabal

Extraction of Silver From Ag-Rich Complex Sulfide Ore 269
Z. Jin, L. Wang and W. Liao

Investigating the Behavior of Iron Solid Products During
Direct Acid Leaching of Limonitic Laterites 275
D. Georgiou, P. Perdikis and V. G. Papangelakis

Removal of Heavy Metals

RECOVERY OF URANIUM USING

CONTINUOUS COUNTERCURRENT ION EXCHANGE (CCIX™)

Joseph C. Milbourne[1] and Irwin R. Higgins[2]

[1]Tetra Technologies, Inc.
25025 I-45 North
The Woodlands, Texas 77380
and
[2]Tetra Technologies, Inc.
140 Mitchell Road
Oak Ridge, Tennessee 37830

Abstract

Tetra Technologies' CCIX™ (continuous countercurrent ion exchange) system has been involved in a wide range of uranium concentration, separation and purification applications over the past 40 years. Uranium ion exchange applications have ranged from the treatment of copper heap leach solution containing 5 parts per million of uranium to the treatment of high strength sulfuric acid solutions containing several thousand parts per million of uranium. The flexibility and the countercurrent mode of operation and other unique features of the CCIX™ have resulted in successful uranium recovery from these solutions and many others.

Separation Processes: Heavy Metals, Ions and Minerals
Edited by M. Misra
The Minerals, Metals & Materials Society, 1994

此为试读,需要完整PDF请访问: www.ertongbook.com

Introduction

The recovery, purification and separation of uranium from solution using ion exchange resin is well known. Uranium is particularly well suited for processing and recovery using ion exchange due to resin's high selectivity for uranium. Uranium forms a wide range of naturally occurring species[1] and can be recovered as either an anion or cation. The selection of the proper ion exchange process depends on the nature of the uranium solution to be treated and the desired form of the concentrated uranium.

Background

Uranium recovery and purification technology using ion exchange has evolved considerably from its beginning in the nuclear era of the mid 1940's through the 50's, 60's and 70's when domestic uranium production peaked. However, the decline in the domestic production of uranium in the 1980's has left a void in the development of new ion exchange technology for the recovery of uranium. Tetra Technologies' CCIX™ (Continuous Countercurrent Ion Exchange) system was developed in the early days of uranium recovery and has evolved considerably since that time. This paper will review the unique features of the CCIX™ system and will describe some of the uranium recovery applications where CCIX™ has been applied.

Continuous Countercurrent Ion Exchange (CCIX™)

The selection of ion exchange equipment to be used for uranium recovery is as important as the type of resin selected. Continuous countercurrent ion exchange or CCIX™, has significant advantages over conventional fixed bed ion exchange systems.

These advantages include: more efficient utilization of resin due to the packed bed counter current configuration; stronger product streams; and less waste solution due to the intrinsic efficiency of displacement rinsing between loop sections. Additionally, the CCIX™ system allows greater flexibility in treating high ionic strength solutions due to the ease of resin transfer.

The Higgins Loop Countercurrent Ion Exchange System (CCIX™) consists of a packed bed of ion exchange resin in a closed loop made up of reacting sections which are separated by butterfly valves. These butterfly valves are fitted with special "wiping" edges that prevent the crushing of resin as the valve closes. Both the loading and regeneration reactions are performed simultaneously in the loop. A schematic of a CCIX™ contactor is shown in Figure 1.

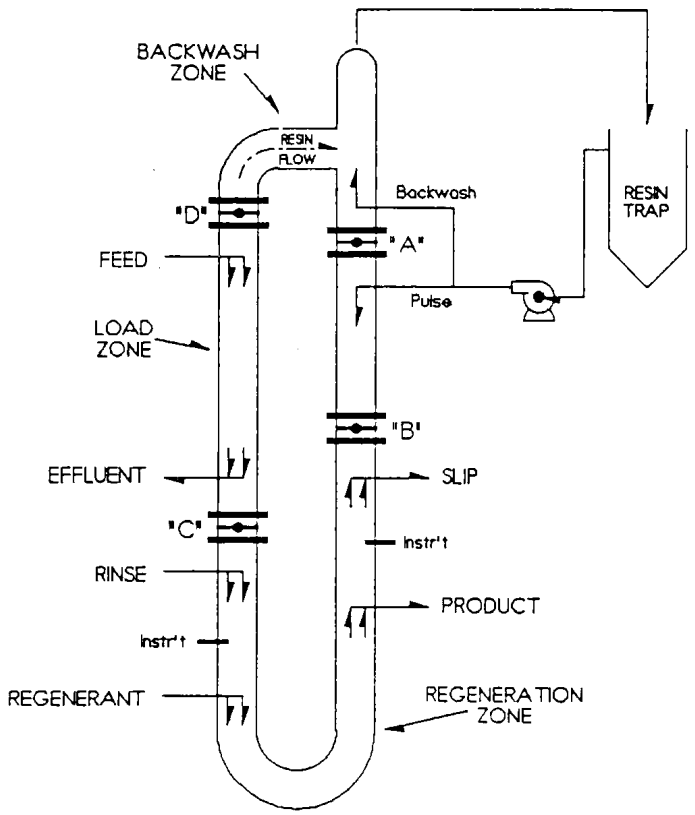

Figure 1 - Schematic Drawing of a CCIX™ showing the various operating sections

Operation of CCIX™

The CCIX™ system operates in a counter current mode so that in the loading section of the vessel, feed solution firstly contacts the most highly loaded resin as the feed enters the loading chamber. As the feed passes through the load section it contacts resin that is less and less loaded. Finally, the treated solution exits the loading zone through screened collectors. This countercurrent mode of operation results in maximum resin capacity utilization.

The countercurrent operation in the regeneration section of the vessel allows strong regenerant to contact the least loaded resin first and thereby insures efficient regeneration. As the regenerant passes through the regeneration section of the vessel, it contacts more and more highly loaded resin so that when the regenerant exits the vessel through screened collectors it is in contact with the most highly loaded resin. Regeneration is often accomplished by using a void volume displacement. The normal operating configuration of the CCIX™ unit is shown in Figure 2.

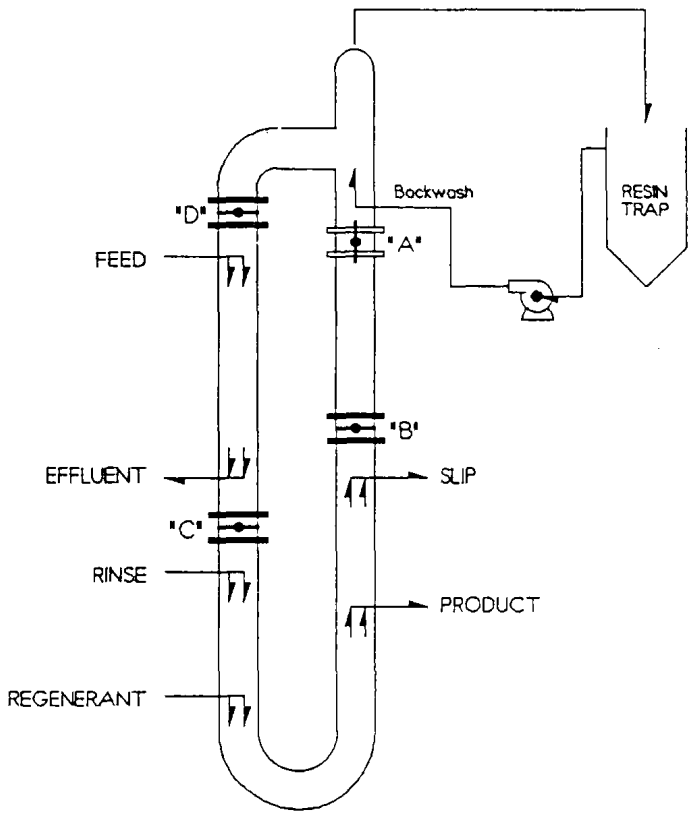

Figure 2 - CCIX™ in the Normal Operating Mode

A major source of excess waste volume generated by conventional fixed bed ion exchange systems is rinse solution. In fixed bed systems, rinsing requires several bed volume displacements. As a result, large volumes of waste solutions are generated. In contrast, CCIX™ accomplishes rinsing between loop sections by void volume displacement. The amount of rinse is controlled by means of a conductivity probe located between the regeneration and loading sections of the loop. Rinse solution pushes the regenerant down to a position at the conductivity probe. This very efficient rinsing is also aided by the solution density difference between rinse and regenerant solutions.

Feed solution is treated in the load section for a predetermined period normally 3 - 5 minutes. After this time, the feed to the loading section is momentarily diverted from the system and resin is transferred. A hydraulic pulse of solution causes loaded resin to move from the loading section to the regeneration and back washing section and fresh regenerated resin to move from the regeneration section to the loading section. This entire operation normally takes 30 - 45 seconds to complete. Figure 3 shows the position of the various valves during the resin transfer mode.

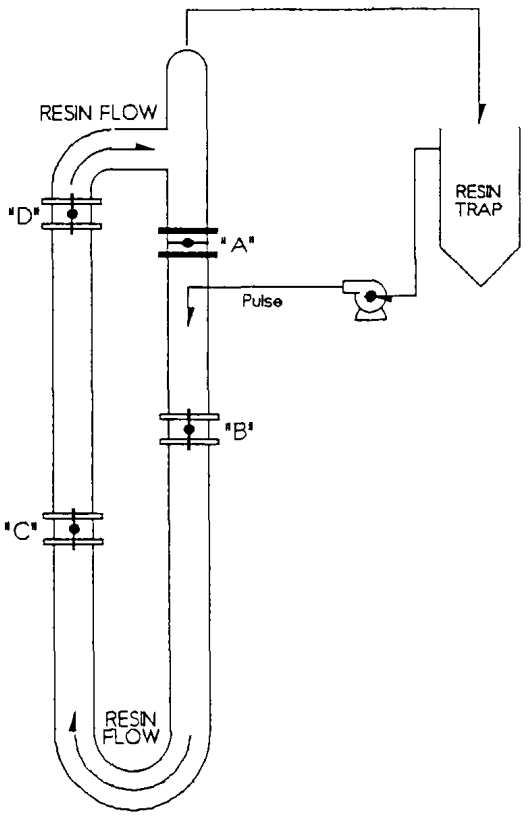

Figure 3 - CCIX™ in the Resin Transfer Mode

After the resin transfer operation is completed, the loop is returned to the normal service mode and both feed and regenerant are reintroduced to the loop. The frequent cycling and back washing of resin allows the CCIX™ to tolerate small quantities of solids in the feed. These solids as well as broken resin beads are backwashed out of the system during every transfer cycle.

Uranium Recovery Applications Using Ion Exchange

Ion Exchange for uranium recovery from fission products (1946 - 1949)

Prior to the development of strong base resins in the late 1940's, spent reactor fuel elements were leached with strong nitric acid to form solutions containing fission products and uranium. These solutions were then treated using sulfonated phenolic cation exchange resins, first introduced by Rohm & Haas as IR-100, to adsorb the fission products and uranium. Later, other resin manufacturers introduced phenolic cation resins (Permutit Zeo-Karb 315; Duolite C-3 , Dow's Dowex 30 Farbenfabriken Bayer's Lewatit KS). Selective recovery of the fission products and uranium was achieved by using a selective elution technique first developed at Oak Ridge National Laboratory (ORNL) and later described by Spedding[2] in his detailed work in the separation of rare earths.

Although many elements in the nitric acid solution exhibited similar affinities for the resin, each element had a unique affinity for the complexing agent used to elute the resin. This feature allowed the use of cation resin for the separation of uranium from fission products. Uranium was selectively eluted from loaded phenolic resin using a mixture of citric acid and ammonium citrate at carefully controlled pH. Other fission products were eluted by varying the pH and strength of the citric acid.

Various complexing agents in addition to citrate have been evaluated for this type of elution including: EDTA, tartic acid, lactic acid, sulphosalicylic acid, ethyl acetoacetate and acetyl acetone. Spedding's work on rare earth separation[3,4] illustrates the use of these complexing agents.

After the introduction of Dowex 50, a strong acid sulfonated styrene divinylbenzene cation resin in late 1949, the final elution of fission products was achievable using nitric acid.

Homogenous Reactor Processing (1953)

The Homogenous Reactor was a chemist's delight. Enriched uranium sulfate was dissolved in deuterium oxide (heavy water). The fuel, the moderator, and the heat exchange media were homogenous. Operation of the reactor required that after one day's operation, 20 % of the fuel was to be removed from the reactor and allowed to cool for one day. The fission products decayed rapidly after one day and were recovered using cation exchange resin. Removal of the fission products was necessary because of their high neutron cross sectional area which retards the fission reaction. Neutron adsorbing xenon-135, a nobel gas, was also bled off and recovered on activated carbon.

Cation exchange resin worked well to remove most of the fission products, rare earths, barium, strontium and cesium. This work revealed the ion exchange behavior of metals not previously encountered. The work also prompted the development of the CCIX™ in an attempt to minimize radiation damage to the ion exchange resin. The highly radioactive fission products severed the sulfonate and amine groups from the polymeric backbone of the resin resulting in loss of capacity.

The project was short lived due to many factors including the safety hazards associated with mobil highly radioactive fission products in the liquid phase and the relatively low operating temperature of the reactor.

The Wet Method for Conversion of Uranyl Nitrate to Uranyl Fluoride (1951)

The first application of CCIX™, invented in 1951 and later patented in 1957[5], involved the cation conversion of uranyl nitrate, $UO_2(NO_3)_2$ to uranyl fluoride, UO_2F_2 using Dowex 50, 50 X 100 mesh, 12 % cross linking. The wet method was designed to be an alternative to the dry process. The dry process involved roasting enriched uranyl nitrate to form UO_3 and then fluorinated the UO_3 with anhydrous HF in an Inconel reactor to form UF_4. The wet method involved adsorption of the uranyl cation, UO_2^{+2}, on strong base styrene divinylbenzene resin and then eluting the loaded resin with hydrofluoric acid. The adsorption and elution reactions are as follows:

Adsorption:

$$UO_2(NO_3)_2 + 2RH \rightarrow R_2UO_2 + 2HNO_3 \qquad (1)$$

Elution:

$$R_2UO_2 + 2HF \rightarrow 2RH + UO_2F_2 \qquad (2)$$

Where R represents the resin.

The pregnant eluant containing UO_2F_2 could then be converted to UF_4 slurry in an electrolytic cell with a mercury cathode and a platinum anode. The high purity UF_4 would become feed material to the gaseous diffusion plant or feed stock to make fuel. The wet process produced a purer UF_4 product than the dry process due to slight corrosion of the Inconel reactor in the dry process.

Treatment of Bomb Liner Scrap (1952)

Shortly after the development of the first strong base anion exchange resins, Rohm & Haas' IRA 400, Dow's Dowex 1, Permuitit's De-Acidite-FF and Farbenfabriken Bayer's Lewatit M-2, one of the most important discoveries in the extraction of uranium was made: uranium formed stable anionic complexes that exhibited a high selectivity for anion exchange resin.

The first use of CCIX™ and strong base resin was in the treatment of the bomb liner scrap. As a point of clarification, bomb liner refers to the reduction apparatus by which uranium metal was made, not the residue from the manufacture of thermonuclear bombs. Uranium metal was manufactured by combining UF_4 and magnesium metal in a magnesium oxide-lined steel reduction "bomb" [6]. An external heat source was applied to initiate the reaction and uranium metal was formed by the following exothermic reaction:

$$UF_4 + 2\,Mg^0 \rightarrow U^0 + MgF_2 \qquad (3)$$

Following the reaction, an ingot of pure uranium metal was formed in the bottom of the bomb. The magnesium fluoride residue, containing small amounts of uranium, is referred to as bomb liner scrap.

The first treatment process for the recovery of uranium from bomb liner scrap involved the dissolution of the scrap in carbonate leach using potassium permanganate as an oxidant. The resulting uranyl tricarbonate anion, $UO_2(CO_3)_3^{-4}$, was recovered using strong base ion exchange resin. The adsorption reaction can be described as:

Adsorption:

$$UO_2(CO_3)_3^{-4} + 4RNO_3 \rightarrow R_4UO_2(CO_3)_3 + 4\,NO_3^- \qquad (4)$$

The uranium loaded resin was eluted using a mixture of ammonium nitrate and nitric acid. The elution reaction can be described as :

Elution:

$$R_4UO_2(CO_3)_3 + 4\,NO_3^- \rightarrow UO_2(CO_3)_3^{-4} + 4RNO_3 \qquad (5)$$

Where R represents the resin.

The pregnant eluate was then acidified with nitric acid, and treated with ammonia to precipitate ammonium diuranate.

此为试读,需要完整PDF请访问: www.ertongbook.com