Ion Exchange and Sorption Processes in Hydrometallurgy

Edited by M. STREAT and D. NADEN
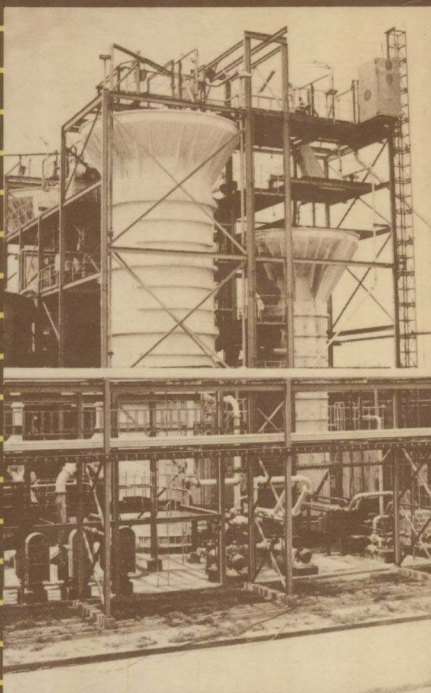
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Introduction

The progressive application of ion exchange and sorption technology in the field of hydrometallurgy has been most spectacular in the last 15–20 years. This is no doubt partly due to the advent of successful continuous ion exchange technology and the development of new selective polymeric ion exchange materials and the fabrication of durable adsorbents such as activated carbon.

Separation processes based on sorption are not energy intensive and can thus be applied to low-grade mineral resources and to byproduct recovery of valuable metals. In this respect, the process technology is similar to solvent extraction which has been so successfully applied to the recovery and purification of base metals such as copper.

Ion exchange and sorption have much in common, since the former is based on the distribution of soluble ions between an aqueous solution and a reactive polymer containing selective ligands. The process is governed by stoichiometry and electrical neutrality and equilibrium shifts are produced by changes in chemical potential. Sorption of ions from aqueous solution into naturally occurring and synthetic porous solids is dominated by the surface chemistry and physics of the porous medium. Equilibrium sorption and desorption similarly depend on the external solution concentration, though there is less fidelity in control of the selectivity of the sorbent. Both ion exchange and sorption have found widespread use in the recovery, separation and purification of metals, the most notable advances having occurred with uranium, precious metals and the platinum group metals.

Uranium is recovered from the naturally occurring ore body by wet chemical methods, including leaching, ion exchange, solvent extraction and precipitation. Alternatively, uranium can be obtained as a byproduct in the recovery of gold or separated from wet process phosphoric acid. The combination of ion exchange and solvent extraction is very powerful and enables uranium to be recovered from very low solution concentration, often in the region of 100 ppm, with sufficient selectivity to yield a final product containing less than about 100 ppm of metallic impurities. One of the principal advantages of solid phase recovery processes is the ability to recover metal values directly from solutions containing suspended solids. In addition, the development of continuous countercurrent ion exchange equipment in the form of multistage fluid beds, for recovery from solutions with a low suspended solids content, and stirred vessels in horizontal arrangement, for recovery from leach pulps, has established this technology as a foremost advance in hydrometallurgy. There are strong incentives to modify and adapt continuous solid–liquid processes into new areas of application, and this is now evident in the rapid introduction of continuous processes into gold sorption

on to carbon particles. The use of adsorption to recover gold at trace levels in cyanide solutions has made an enormous impact on gold recovery flowsheets. The application of ion exchange in uranium extraction and the recovery of gold from aqueous solutions with activated carbon are reviewed in this book. The science and technology of these processes have not been reviewed so comprehensively in any other text.

The demand for platinum group metals (PGM) is unrelenting and has been boosted by the need to produce catalysts for the production of gasoline from coal and the production of chemical intermediates by Fischer–Tropsch reactions. PGM concentration in aqueous solution is usually low and this has prompted much research in the field of solvent extraction to tailor-made extractants with platinum-selective ligands. This work has recently been extended to polymeric ion exchange materials with chelating ligands capable of separating the PGMs in dilute aqueous solution. The chapter on PGM extraction reviews the synthesis of reactive polymers, the chemistry of the separation process and also details the process aspects of a total flowsheet for the separation and recovery of the PGMs. The review draws together much of the diverse work that has been published in the literature in recent years. The future of ion exchange in hydrometallurgy will depend on the development of selective chelating adsorbents targetted for particular process applications. Enormous advances in polymer chemistry and the associated organic chemistry have taken place in recent years to meet the growing interest in chelating ion exchangers. The careful design of polymeric structures containing nitrogen, sulphur, phosphorus, nitrogen and oxygen and macrocyclic oxygen ligands have led to many promising ion exchange materials capable of application in hydrometallurgy and related industrial activities. The chapter on chelating ion exchangers is a comprehensive review of the state of the art in this field, the prolific research being exemplified by the 217 cited references.

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Symbols

c	solute concentration in solution
$\bar{c}$	solute concentration in resin phase
C	total solution concentration
$\bar{C}$	resin phase capacity
D	diffusion coefficient of solute in solution phase
$\bar{D}$	diffusion coefficient of solute in resin phase
f	fractional transfer of resin in CIX column
$f_j(x, t)$	resin conversion distribution function for stage j
k	rate constant for particle diffusion control
k_L	rate constant for liquid film control
k_1, k_2	pseudo liquid film mass transfer coefficients with respect to solution and resin phase
N	number of discrete conversion levels in the range 0–1
$P_j(y_i)$	probability of finding resin at conversion y_i in stage j
r_0	particle radius
$r(x, c_j)$	the rate of sorption of resin at conversion x from solution c_j
R	resin flowrate
S	solution flowrate
t	time
v	particle settling velocity

x	Symbols
V_j	volume of stage j in simulation model
V_s	actual volume of a stage in CIX column
X	resin phase conversion
x	composition of solute in solution phase
y	composition of solute in resin phase
δ	liquid film thickness
ε	porosity
μ	solution viscosity
ρ_r	resin phase density
ρ_s	solution phase density
τ	residence time in stage j

Subscripts

B	Barrens concentration
E	eluted resin concentration
F	liquid feed concentration
i	conversion level
j	stage j
j-1	stage j-1
L	loaded resin concentration

Constants

a, b	constants in Langmuir-type equilibrium relationship
p, q, r, s	constants in generalized equilibrium relationship

Contents

v

1 Ion exchange in uranium extraction

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1.1 General introduction

Annual uranium production has risen steadily since 1975 and reached a record
level of 44 000 tonnes in 1981. The latest trend was downwards and the planned
level of production was expected to be about 38 000 tonnes in 1983. The main
reasons for the decrease are cutbacks in production and the closure of mines and
production centres, mainly in the United States. The major uranium-producing
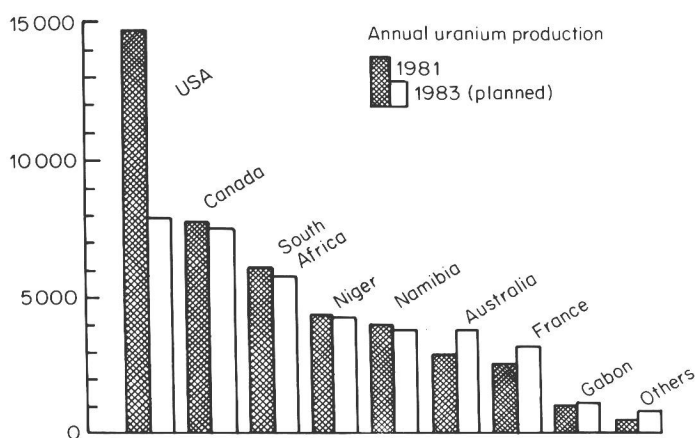countries are given in Figure 1.1.

Figure 1.1 Uranium production capability (1981–3).

Naturally occurring ore-bodies contain about 100–1000 ppm uranium. As these resources become depleted there is increasing interest in recovery from low-grade secondary mineral deposits. It is difficult to process low-grade mineral and produce an ore concentrate at an economic cost. Increases in the cost of labour, fuel, etc., militate against economic uranium production. Seventy per cent of total uranium production costs can be attributed to exploration and mining with the remainder allocated to chemical processing. Chemical processing is energy intensive (crushing, grinding, liquid–solid separation) and requires reagent consumption (leaching, ion exchange, solvent extraction). The important chemical separation processes are ion exchange and/or solvent extraction. The earliest uranium separation process depended on the postwar development of polymeric ion exchange resins containing anion exchange functional groups. In the 1960s, it was found that analogous liquid reagents, e.g. long chain aliphatic tertiary amines, were even more effective for uranium separation, since they are more selective and solvent extraction equipment has the advantage of continuous countercurrent operation. This brought about a revolution in uranium production technology and for many years solvent extraction was preferred to resin ion exchange in the uranium recovery plants in the United States, South Africa and Australia. The development of continuous countercurrent fluid bed resin ion exchange, which combined engineering and operating simplicity with the ability to recover uranium from solutions containing suspended solids, enabled this technology to take the lead as the preferred recovery process. Solvent extraction developments have, however, recently taken place which allows this technology to operate using dirty feed solutions and ion exchange no longer holds a unique position. The long-term future for solid ion exchange technology, whether based on resins or other solid extractants, lies in the major reduction in costs, which can be achieved by the development of compact and easily operated in-pulp recovery processes. This is an area where it has unique advantages over competing processes and where other extraction techniques will find it difficult to follow.

The recovery, purification and concentration of uranium and recent advances in ion exchange technology are surveyed here. The impact of ion exchange technology on uranium recovery from ore is summarized and the importance of preparing the pregnant feed solution for the appropriate ion exchange process is discussed. The selection of ion exchange resins is described together with the relevant background chemistry of the ion exchange separation of uranium. Ion exchange equipment and process design techniques are reviewed, with particular emphasis on continuous ion exchange. Information is provided to enable the process engineer to obtain the required test data and to carry out an empirical design of a typical continuous countercurrent multistage contactor. It is impossible to include all the details of test procedures and process design in a short review of this type, but adequate references are given to enable practitioners to obtain the required information and, possibly, to develop improved design techniques.

1.2 Interactions of the uranium recovery flowsheet and the ion exchange process

1.2.1 The uranium recovery flowsheet

(a) Uranium recovery from milled ore The various flowsheets for the recovery of uranium from milled ores in the United States by both acid sulphate and carbonate leaching have been comprehensively described by Merritt[1] and more general flowsheets have been summarized by Burkin[2]. The role of solid ion exchange in the recovery process and the influence of ion exchange on flowsheet costs is discussed in the following sections.

(i) Acid sulphate leach of conventional ores The postleach stages in the acid leach flowsheets in which liquid (SX) and solid (IX) extraction processes were first used are:
1. Solid-liquid separation and washing of leached ore to recover the dissolved uranium values, using either filtration or countercurrent decantation (CCD).
2. Solution clarification.
3. Uranium extraction by SX or packed bed IX.
4. Uranium precipitation using ammonia or H_2O_2.
5. Solid product drying and packaging.

The first generation of solvent extraction (SX) and solid ion exchange (IX) equipment required solution clarification in order to minimize organic losses in SX and bed blocking in packed bed IX. The drive towards reducing uranium production plant costs and operating costs, as well as the need for flowsheet simplification, led to the recognition of the need to adapt the extraction processes to enable uranium to be recovered from solutions containing suspended solids. Fluid bed ion exchange was the first development to succeed in this aim and this led to the adoption of fluid bed IX equipment and processes in the mid-1970s. Solvent extraction engineering and equipment developments have subsequently led to the commercial acceptance of equipment for treating solutions containing up to 500 ppm solids and SX has again taken the lead in this field[3].

The postleach section of the flowsheet accounts for approximately 40–50 per cent of the cost of the whole flowsheet while the solid–liquid separation and solids washing section accounts for approximately half this value. The elimination of solid–liquid separation and slimes washing by countercurrent decantation or filtration will therefore reduce the cost of the whole flowsheet by 20–25 per cent[4]. The recovery of uranium from the slimes stream or directly from leach pulps by resin-in-pulp (RIP) processes has the potential, therefore, to achieve a significant capital cost reduction. Solid ion exchange has a unique role in this field and one which SX is unlikely to challenge in the near future. Solid ion exchange, through the development of strong resins with good extraction properties and the development of compact, low-cost reliable equipment, has therefore an important place and a long future in the recovery of uranium. The same considerations also apply to other metals.

Phosphate ores are leached by sulphuric acid in order to produce phosphoric acid which is substantially free of ore particles. Phosphate ores can contain from 0.005 to 0.02 per cent of uranium which is leached and reports with the phosphoric acid where it may be found at concentrations up to 200 ppm. Uranium recovery by solvent extraction has been the only feasible recovery technique until recently. Solvent extraction processes usually require treatment of feed acid to remove humate present in the ore, which leads to crud formation and excessive organic losses and treatment of SX raffinate acid to remove organics which would damage the downstream evaporator rubber lining. These two stages contribute approximately 50 per cent to the process capital cost and uranium production cost. Following the decline in the uranium selling price, the cost of recovery by SX becomes prohibitively high and an important source of uranium was neglected.

Recently, however, the use of resin ion exchange has been investigated[5] and a process based on a commercially available amino phosphonic acid chelating resin (Duolite ES467) has been developed and has been piloted on a commercial phosphoric acid plant[6]. The resin process eliminates the need for both feed and product acid cleanup and effectively reduces uranium costs from this source by 50 per cent.

Low-grade phosphate ores also exist that can contain much higher concentrations of uranium than those normally used for phosphoric acid production and a resin ion exchange process will make recovery of uranium from this treatment much more economically attractive.

(ii) Carbonate leach Uranium recovery is usually achieved by either direct precipitation from clarified solutions or by resin extraction from desanded pulps by resin-in-pulp (RIP) procedures (see Section 1.4.4). Solvent extraction has no role in recovery from carbonate solutions owing to the adverse chemistry.

RIP processes are normally used because of the poor settling characteristics of ores which have been subjected to carbonate leaching. The development of improved equipment in the mid-1970s significantly decreased the capital and operating costs as well as improved the recovery of uranium from carbonate leach pulps.

(b) Solution mining The recovery of uranium by direct underground contact of leach solution with the ore, either by *in situ* leaching or stope leaching, results in dilute solutions containing as little as 20 ppm or as high as 200 ppm U_3O_8 with a low solids content. Both acid sulphate and carbonate leach have been used in these processes[7] and uranium recovery has been achieved by both packed and fluid beds. Leach solutions pumped into porous ore bodies must have a very low solid content in order to minimize the reduction of ore porosity, and packed bed ion exchange can therefore be safely used.
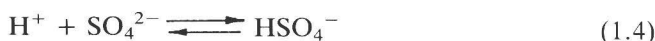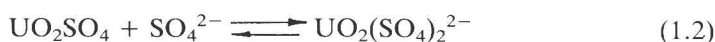
Solvent extraction has not found a use in this case as the leach solutions are often carbonate and are usually dilute.

1.2.2 Uranium leach chemistry

(a) Introduction As the chemistry of uranium leaching has been extensively described by others[1] a further detailed description is not appropriate. The features of leaching that will effect the subsequent ion exchange recovery step will, however, be briefly discussed.

(b) Sulphuric acid leaching In a normal acid leaching process milled uranium ore is agitated at atmospheric pressure with sulphuric acid at temperatures up to 80 °C for approximately 24 hours in the United States where sandstone ores predominate and for periods up to 48 hours in Canada and South Africa where the ore is more refractory. Higher pressure leaching at higher temperatures may be used in some cases. Acid addition varies from ore to ore but in general the aim is to achieve a final pH of approximately 0.5–1.5 to prevent reprecipitation of the uranium.

Uranium forms anionic sulphate complexes in the VI oxidation state in acidic aqueous sulphate solutions. In the absence of other anion-forming impurities, the complexes of uranium, bisulphate and sodium sulphate can be written as follows:

$$UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4 \qquad (1.1)$$

$$UO_2SO_4 + SO_4^{2-} \rightleftharpoons UO_2(SO_4)_2^{2-} \qquad (1.2)$$

$$UO_2(SO_4)_2^{2-} + SO_4^{2-} \rightleftharpoons UO_2(SO_4)_3^{4-} \qquad (1.3)$$

$$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^- \qquad (1.4)$$

$$2Na^+ + SO_4^{2-} \rightleftharpoons NaSO_4 \qquad (1.5)$$

where Na^+ represents the cation content of the ore. Reaction 1.4 occurs at the acid concentration which is normally achieved in the last stage of leach. Both HSO_4^- and SO_4^{2-} will be present in acid sulphate leach solutions and will compete for sites on an anion exchange resin, particularly the bisulphate ion. A high concentration of sulphate promotes reaction (1.3), leading to the formation of the tetravalent complex which is the predominant species adsorbed by strong base resins at pH 1.5–2.0[1]. At higher acid concentrations reaction 1.4 is promoted and competition for resin sites is increased.

The maintenance of proper oxidizing conditions during leaching is particularly important in order to achieve high uranium recovery. Oxidizing agents may be chosen from a wide range, including manganese dioxide (pyrolusite), ferric ion,