The benefits of heavy resins in fluidized-bed ion-exchange columns

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SYNOPSIS

The advantages to be gained from the use of a high-density ion-exchange resin in a uranium-recovery circuit are shown. It is concluded that, in existing fluidized-bed plants, the throughput of solution can be increased by up to 40 per cent at the same uranium recovery. Alternatively, the values in the barren solution can be improved at the same flow-rate of solution.

SAMEVATTING

Die voordele van die gebruik van 'n hoë digtheid ioonuitruilingshars vir uraanontginning word bepaal. Die gevolgtrekking word gemaak dat die toevoer van die oplossing in die bestaande fluiedbed aanlaes verhoog kan word met tot 40 persent terwyl die uraanherwinningsvlak behou word. Alternatiewelik kan verbeterde herwinningsvlakke behaal word met die oplossing se bestaande vloeitempo's.

Introduction

The development of the ion-exchange systems currently used in South Africa for the recovery of uranium were initiated by the need for a system that would concentrate the low values in the liquors resulting from the leaching of low-grade ores.

In most of the uranium circuits employing ion exchange, the resins perform a preconcentration duty, which then allows a smaller solvent-extraction plant to be built into the overall circuit than would otherwise be required. In the design and operation of an ion-exchange plant, the objective is the simultaneous satisfaction of the following two criteria: the highest possible throughput of leach liquor and the highest possible recovery of uranium from the leach liquor. Unfortunately, a certain measure of compromise must be achieved, for the two work counter to each other and cannot be maximized simultaneously.

The throughput in a fluidized-bed ion-exchange column is determined by the physical size of the column and the hydrodynamic properties of the resin and solution, while the degree of uranium recovery is controlled by the mass-transfer characteristics of the resin and solution.

The symbols used are defined in the nomenclature at the end of the paper.

Hydrodynamic Properties

The fluidization level of resin depends upon the following:
(a) the physical size of the resin beads,
(b) the viscosity (μ) of the solution, and
(c) the difference in density ($\triangle\rho$) between resin and solution.

Size of the Beads

The current resin-manufacturing process produces beads within a certain size range, generally 0,2 to 0,8 mm. In any given fluidizing solution, beads of this size range will undergo different levels of fluidization for each particle size. The level of fluidization of a log-normally distributed range of particle sizes can be related to a mean diameter calculated from the size distribution, and this mean diameter can be used in the prediction of the fluidization properties of a resin.

Viscosity and Density of the Solution

These two properties of the solution in a particular uranium-recovery plant are dependent upon the flow-sheet, for both the concentration of the solids in solution and their levels raise the density and viscosity.

Density of the Resin

The density of the resin is a function of
(i) the manufacturing process employed,
(ii) the type of counter ion loaded onto the resin, and
(iii) the degree of counter-ion loading.
In uranium ion-exchange plants, the density of the resin changes during the extraction step, but it is the lowest resin density that determines the plant-operating characteristics.

Numerous correlations have been proposed for the prediction of the fluidization of spherical particles by liquids in annular beds. The correlation that was found to best predict the fluidization of resin is that proposed by Ramamurthy and Subbaraja[1]. These authors correlated the Galileo number (Ga) with the particle Reynolds number (Re_p) and the drag force C_d in the laminar, intermediate, and turbulent flow regimes. With the resins and fluidization levels currently used, Re_p falls into the intermediate region, and the relevant correlation is

$$Ga \ .. \ 13,9 \ (Re_p)^{1,4} \ (\phi_e)^{2,21}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

By the rearrangement of the correlation of Ramamurthy and Subbaraja, the superficial velocity can be calculated as a function of the porosity of the fluidized bed, and the hydrodynamic properties of the resin and the solution. The porosity of the fluidized bed can, in turn, be related to bed expansion through the following:

$$BE \ = \ \frac{\epsilon - \epsilon_s}{1 - \epsilon_s}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Where ϵ_s is the porosity of the settled bed ($\epsilon_s = 0,4$ for anion resins), and BE is the fractional bed expansion.

In Fig. 1, experimentally determined fluidization curves for a conventional resin and SENBRIX high-density resin, both in sulphate form, are compared with those predicted from the above correlation. The fluidizing medium used was a typical clarified uranium leach liquor.

With a correlation of the type presented, it is possible to compute the effect of a variation in solution and resin properties on the fluidization levels in an ion-exchange column. The hydrodynamic advantages of a heavy resin

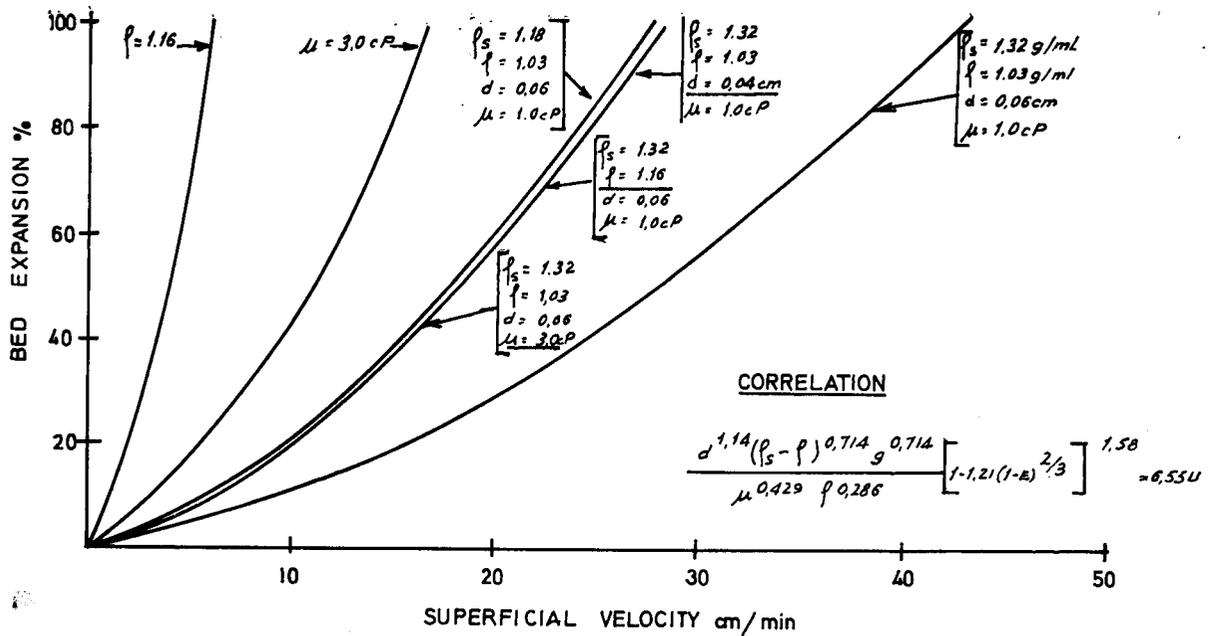* Sentrachem Limited, P.O. Box 61204, Marshaltown 2107, Transvaal.

Fig. I—Curves of bed expansion for resins in the sulphate form

are immediately evident from the curves presented in Fig. 1.

If the constraint on the upper limit of fluidization in a continuous ion-exchange column is a bed expansion of 100 per cent, the replacement of a conventional resin ($\rho = 1{,}18$) with a high-density resin (SENBRIX $\rho = 1{,}32$) allows the throughput through a column of a given diameter to be raised by 59 per cent, on the assumption that all the other hydrodynamic properties are held constant. Alternatively, throughput and fluidization can be held constant, while

  (i) the viscosity of the solution is increased threefold, or
  (ii) the density of the solution is increased by 0,13, or
  (iii) the mean diameter of the beads is reduced by 33 per cent.

A marginal change in all three of the above achieves the same result.

In terms of hydrodynamics, a high-density resin provides greater design and operating flexibility. In certain circumstances (e.g., in solutions of high density or viscosity), continuous ion exchange can be achieved only with denser resins.

Mass Transfer

The extraction and recovery of uranium from a leach liquor depend upon high levels of mass transfer from solution to resin in the loading step, and from resin to solution during the elution. If recovery and throughput are to be maximized simultaneously, the mass-transfer rates must be high.

The rate-controlling step between the uranium in the solution and that on the resin exists either in diffusion of the charged molecule across a postulated Nernst film surrounding the resin bead (film-diffusion control), or diffusion within the pore structure of the bead (particle-diffusion control). The driving force causing the mass transfer is the concentration gradient between solution and resin.

Film Diffusion

According to the resistance concept (of Treyball), the rate of exchange is a function of the mass-transfer coefficient, the area for mass transfer, and the concentration gradient across the film. It can be expressed as

$$\text{Rate} = Ka\ (Cf - C^*). \qquad (3)$$

In general, film diffusion controls when concentrations in the solution phase are low. In the operation of continuous ion-exchange for the extraction of uranium, film control occurs in probably all but the bottom stage of a column being fed with a liquor that has a uranium tenor of 0,25 g/ l. At lower tenors, all the stages are controlled by film diffusion.

Naturally, the thickness of the liquid film surrounding the resin bead determines the distance through which diffusion has to take place. This thickness is, in turn, dependent upon the shear forces around the bead, which, again, depend upon the hydrodynamic conditions under which the exchange is operated. The mass-transfer coefficient is a measure of all these interrelated factors, and is thus correlated in equations of the following type:

$$Sh = c\ (Re)^{\frac{1}{2}}.\ (Sc)^{\frac{1}{3}} \qquad (4)$$

Particle Diffusion

Particle diffusion is controlled by the net rate of movement of the uranyl and sulphate molecules within the pores of the resin beads. The movement rate or diffusivity of the molecules depends upon the pore-size distribution within the resin beads, and, if this remains constant from one resin to another, so too will the diffusivity remain constant.

The area through which the molecules have to migrate within the resin influences the overall rate of the reaction; the smaller the area, the quicker will they reach their destination. Thus, the rate of exchange controlled by particle diffusion can simplistically be predicted by

$$\text{Rate} = \frac{D_p}{r^2}\ (C^* - Cs) \qquad (5)$$

Particle diffusion controls the overall exchange rate only when film diffusion occurs rapidly. Consequently, this rate-controlling step applies when the concentration of the solution is high, as it is during the elution of resin. All stages in a continuous ion-exchange elution column would operate under conditions of particle-diffusion control.

Kinetics

In addition to the factors that control the rate of mass transfer, the effect of the mean particle size on the kinetics of the loading and elution steps has also to be considered. For film-diffusion control, rearrangement of equation (4) shows that the mass-transfer coefficient is inversely proportional to the diameter of the resin bead. A reduction in mean bead size therefore increases the mass-transfer coefficient and the rate of the reaction, all other factors remaining constant. However, if the mean diameter of the bead is reduced, the total area for mass transfer in a given volume of resin is increased. Calculation shows that the ratio of the areas for different bead diameters varies inversely with the ratio of the diameters, i.e.

$$\frac{A_2}{A_1} = f\frac{(d_{p_1})}{(d_{p_2})}$$

Fig. 2 shows the effect of area on the rate of a kinetic curve controlled by film diffusion. For a decrease of 33 per cent in mean bead diameter, a 50 per cent increase in rate (film-diffusion control) is achieved.

The increase in kinetic reactions under particle-diffusion control that results from a reduction in the mean diameter of the bead is greater even than was calculated for film control, for the variation is now a function of the square of the bead diameter. Thus, from equation (5),

$$\frac{R_2}{R_1} = \frac{(d_{p_1})^2}{(d_{p_2})^2} \qquad \ldots \ldots \ldots \ldots \quad (7)$$

The two curves showing elution rate in Fig. 2 demonstrate the advantage gained from a reduction of 33 per cent in mean bead diameter.

Operation of the column

One of the major benefits in the use of a high-density resin is attained when it is used to replace the conventional resin in an existing continuous ion-exchange plant. Should the desire be to improve the recovery of uranium by a reduction in the tenor of the barren solution while maintaining the plant throughput, the mean bead size of a heavy resin can be reduced. As shown in Fig. 1, the same fluidization and throughput are attained with a mean bead size that is 33 per cent smaller.

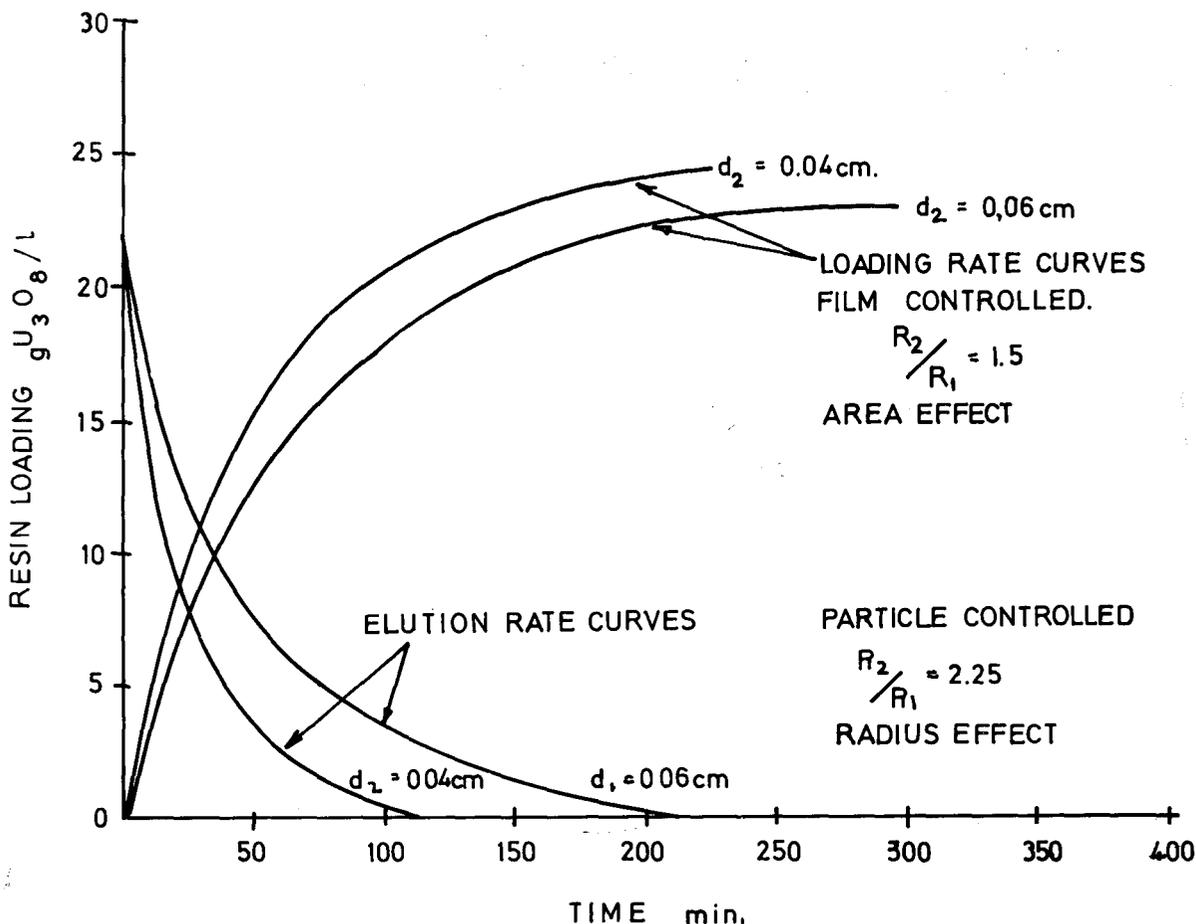By the use of existing models for the exchange

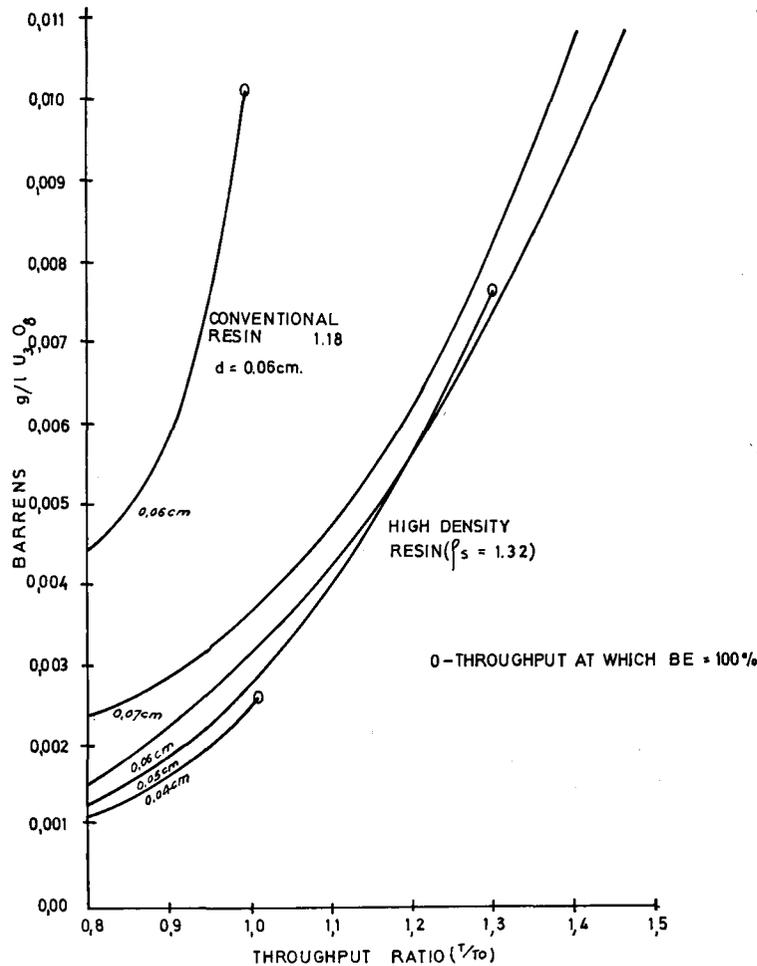Fig. 2—Effect of resin bead size on the loading and elution of U_3O_8

Fig. 3—Comparison of the performance of conventional and high-density resins in continuous ion exchange

occurring in the loading and elution columns of a continuous ion-exchange operation, the composition of the eluted resin and the concentration of the barren solution can be calculated. This was done for the data given in Table I. Certain advantages that accrue from a reduction in the size of the resin beads are immediately obvious from the curves in Fig. 2.

TABLE I

DATA FOR THE CALCULATION OF VALUES ON ELUTED RESIN AND IN BARREN SOLUTION

Loading column	7 stages
Elution column	7 stages
U_3O_8 in pregnant solution	0,25 g/l
U_3O_8 on resin	20 g/l
Bed expansion	100 per cent
Contact time (loading)	62 min per stage
Contact time (elution)	144 min for 7 stages
Flow-rate of pregnant solution	0,276 m³/m² . min
Eluant	10 per cent H_2SO_4

In the elution column, where the total contacting time with the resin is 144 min, smaller resin beads would be completely stripped of U_3O_8, as opposed to the residual 1,2 g/l on conventional resin beads. This lower eluted value immediately results in a reduced tenor in the barren solution because of the more favourable equili-

TABLE II
RESULTS OF CIX COMPARISON

	Conventional resin	High-density resin
Mean bead size (cm)	0,06	0,04
Relative elution rate	1,00	2,25
Relative loading rate	1,00	1,50
U_3O_8 on eluted resin (g/l)	1,20	0,00
U_3O_8 in barren solution (g/l)	0,0101	0,0025

brium that now exists at the top of the loading column. This factor, coupled with the better kinetics that are also being achieved in each stage of the loading column, means a further improvement in the barren solution. Based on a mathematical computation, the expected results are summarized in Table II.

In Fig. 3, the values in the barren solution for the ion-exchange train outlined in Table I are given as a function of the throughput ratio. It was assumed that the upper limit of plant operation is a bed expansion of 100 per cent.

The curves presented in Fig. 3 show that a careful choice of the mean bead diameter of a high-density resin for use in continuous ion exchange can result in im-

provements in either the barren solution or the plant throughput (or both simultaneously).

For the continuous ion-exchange system considered, a fourfold reduction in the concentration of the barren solution is possible at constant throughput. Alternatively, at a constant value of barren solution, the throughput can be raised by as much as 40 per cent.

Conclusions

The use of high-density resins in fluidized-bed continuous ion-exchange columns allows far greater flexibility in plant operation than there is with resins of low density. In existing underdesigned equipment, significant improvements in both throughput and recovery can be achieved. In the design of plants for high-density resins, a lower capital expenditure is incurred, without a reduction in operating efficiency.

Nomenclature

A	area
a	area for mass transfer
c	constant
C_i, C_s	concentration
C^*	equilibrium concentration
C_d	drag force
D_f	film diffusivity
D_D	particle diffusivity
d_p	particle diameter
Ga	Galileo number $\quad Ga = d_p{}^3 \dfrac{(\rho_B - \rho)\rho g}{\mu^2}$
K	mass-transfer coefficient
Re_p	particle Reynolds number $\quad Re_p = \dfrac{d_p U \rho}{\mu}$
r	bead radius
R	rate of exchange
S_c	Schmidt number $\quad S_c = \dfrac{U}{\rho D_f}$
U	superficial fluid velocity
ϵ	fluidized-bed porosity
ϵ_s	settled-bed porosity
ϕ	velocity correction factor $\phi_\epsilon = [1 - 1,21\,(1 - \epsilon)\frac{1}{3}]^{-1}$
μ	viscosity
ρ	solution density
ρ_s	particle density

Reference

1. RAMAMURTHY, K., and SUBBARAJA, K. Ind. Engng Chem. Proc. Des. Dev., vol. 12, no. 2. 1973. p. 184.

Validation of welded constructions

An international conference on the Fitness for Purpose Validation of Welded Constructions is to be held in London from 17th to 19th November, 1981.

The modern concepts of design and fabrication based on the achievement of quality matched to the nature of the service conditions offers both a logical approach to construction and a more economic utilization of resources. The principle of fitness for purpose demands that the prescribed standard of quality is met and that, for example, although defects in the welded joints may be permitted, the maximum size is not exceeded.

Similarly, aspects of design such as joint detail must be assessed in relation to service performance, and the minimum required properties of materials in respect of toughness, corrosion, weldability, wear, and internal defects must be assured. In fabrication, adequate procedures must be established to control quality during manufacture, and the validation of the final construction will involve the application of appropriate inspection and testing routines to prove that the desired quality has been achieved.

In service, the welded fabrication may need periodic checks or monitoring to ensure that it is still safe for service conditions imposed. Comprehensive revalidation may be needed at the end of the original design life.

Fitness for purpose is now an established concept in many fields, and the principle will be continuously expanded to embrace an ever-widening spectrum of engineering. This international conference will present a state-of-the-art review over the whole field of the validation of welded constructions and will prove of value both to current practitioners and to those who may need to become involved in the future.

The topics of the Conference will include the following:

Overall requirements – of government, national quality boards, EEC and international requirements, insurance companies, and users.

Validation of design – stresses, defect tolerance, assessment of joint details in relation to performance, especially fatigue.

Validation of materials – quality assurance, testing for strength, toughness, high-temperature behaviour, weldability, laminations, wear, corrosion, erosion.

Validation of fabrication – inspection and quality assurance, certification, non-destructive testing (especially in relation to critical size assessment).

Validation of final construction – the role of the pressure test; monitoring of surface condition; periodic inspection; surveillance techniques (acoustic, vibration, thermal, strain gauging, optical), monitoring of property changes.

Revalidation at end of original design life.

Assessment of reliability and review of results.

Address all enquiries to The Welding Institute, Abington Hall, Cambridge CB1 6AL, U.K. Telephone: 0023–891162. Telex: 81183. Cables: Weldaserch Cambridge.