The development of continuous fluidized-bed ion exchange in South Africa, and its use in the recovery of uranium

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SYNOPSIS

The status of the South African research and development programme on continuous ion exchange, which was aimed at the technical and economic assessment of that process for the recovery of uranium, is reviewed.

The first phase of this programme, which has now been completed, involved development investigations on various pilot plants and culminated in the successful operation of a large-scale demonstration plant and the incorporation of the system in a number of new South African uranium plants.

This account highlights the engineering aspects and the design fo the system, its adaptation to process flowsheets, and plans for future development.

SAMEVATTING

Die stand van die Suid-Afrikaanse navorsings- en ontwikkelingsprogram in verband met deurlopende ioonuitruiling wat die tegniese en ekonomiese evaluering van daardie proses vir die herwinning van uraan beoog, word in oënskou geneem.

Die eerste fase van hierdie program, wat nou afgehandel is, het ontwikkelingsondersoeke by verskillende proefaanlegginge behels en het uitgeloop op die geslaagde bedryf van 'n grootskaalse demonstrasieaanleg en die insluiting van die stelsel by 'n aantal nuwe uraanaanlegginge in Suid-Afrika.

In hierdie verslag val die klem op die ingenieursaspekte en ontwerp van die stelsel, die aanpassing van die stelsel by prosesvloeidiagramme, en die planne vir toekomstige ontwikkeling.

Introduction

The unit processes for the recovery of uranium that have been applied in South Africa by way of the acid-leaching route are well known, and comprise leaching, solid–liquid separation, concentration and purification of the metal, and precipitation of the product. In the development of these unit operations, the areas that have received most attention up to now are solvent extraction and ion exchange for the concentration and purification step. However, as regards the chemistry, more work has probably been done on the leaching step.

There have been many developments in the concentration–purification process, the original approach being the precipitation of a uranyl phosphate complex with copper metal. This approach was found to be unpractical, but it was discovered at about the same time that uranyl sulphate could be adsorbed onto strong-base anion-exchange resins. Ion exchange was then introduced on a commercial scale using conventional fixed-bed equipment. Since then, the fixed-bed ion-exchange process has been combined with solvent extraction (the Bufflex process[1]) and the direct solvent extraction of pregnant solutions[2] has been introduced — developments that have led to savings in capital and operating costs and to an improvement in the quality of the product.

The advantages of countercurrent contact were recognized very soon after the introduction of the fixed-bed ion-exchange system, and a number of ideas on moving the resin were proposed and patented[3, 4]. These systems are generally referred to as moving-bed systems, and many variations have been proposed for the treatment of water. An important consideration with these systems is that, although countercurrent flow can be achieved, the bed of resin remains tightly packed.

The key to savings of real significance in capital and operating costs lies in the treatment of the concentration–purification process and the solid–liquid separation process as an integrated system. In this way, the whole problem of uranium concentration and purification can be considered in a wider context in that modifications can be introduced that will not only bring about savings in the concentration–purification step but will allow for simplification of the solid–liquid separation step, thereby bringing about further savings.

The use of conventional fixed-bed ion exchange and solvent extraction has placed two major constraints on the solid–liquid separation system.

(1) The clarity of the pregnant solution has to be as high as possible. In ion exchange the use of a packed bed of resin, whether stationary or moving, leads to the blocking of the interstices if the clarity of the solution is poor. Frequent back-washing will thus be required or, in the case of a moving bed, frequent cycling. In solvent extraction, solvent losses tend to be inversely proportional to the clarity of the solution and represent a significant fraction of the operating costs of the concentration–purification step.

(2) The volume of solution produced per ton of solids treated is required to be kept to a minimum. This is because the cost/scale factors of both fixed ion-exchange plants and solvent-extraction plants are generally unfavourable. Furthermore, in the case of solvent extraction, solvent losses can be regarded as proportional to flow-rate.

The fluidized-bed system is inherently more suitable for the treatment of solutions of poor clarity in that it

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allows free passage to fine particles of slime. It therefore formed the basis of the development programme on continuous ion exchange in South Africa, the basic aim of the programme being the relaxation of the previously mentioned constraints, which would permit the introduction and development of alternative routes for solid–liquid separation.

The obvious answer to the problem of these constraints is the complete elimination of solid–liquid separation. However, when this was attempted in South Africa, it was not commercially successful because of major engineering problems.

Historical Aspects

The magnitude of the potential cost savings resulting from the treatment of unclarified solutions has long been realized and is widely accepted. There are, of course, cases where the production of solutions of high clarity is sometimes virtually impossible, and in-slime recovery operations are a necessity as in certain parts of Wyoming in the U.S.A.

The concept of a multiple-stage fluidized-bed column for the treatment of unclarified solutions and slimes containing uranium was suggested as far back as 1955 by Levin[5]. His idea, which did not progress beyond laboratory scale, is basically the same as that which has now been put into operation. It differed in one respect — the method of resin transport. He suggested shutting off the flow of feed and allowing the resin to drain from tray to tray under gravity. This was a good simple idea, but, in terms of what is now known, it is unlikely that this method of resin transport could have been scaled up successfully.

An alternative fluidized-bed system was investigated in Australia at about the same time. This was the jigged-bed system described by Arden *et al.*[6] in 1958. However, this technique suffered from a number of practical operating problems and was never pursued. A similar system was proposed in 1957 in the U.S.A. by Chase[7].

In 1961, Cloete and Streat initiated work at Imperial College on the basic concepts of their reverse-flow idea for the transport of resin in fluidized-bed columns. This led to the acceptance of a British patent in 1967 with a priority date of October 1962[8].

Interest in the multiple-stage fluidized-bed contactor was revived in South Africa in the mid-sixties by Lloyd[9], who suggested countercurrent cyclone washing similar to that described by Arden[6], followed by direct treatment of the cyclone overflow by continuous fluidized-bed ion exchange as a simple uranium-recovery flowsheet. In a subsequent paper[10], Lloyd gave indications of the cost savings that could be expected from the introduction of a slimes process.

In 1968, the National Institute for Metallurgy (NIM) used the work of Cloete and Streat as a starting point in the development of a continuous ion-exchange system that could be applied commercially to the recovery of metals in the hydrometallurgical processing of minerals. Improvements in the design of the column and trays and in the control of the resin inventory were patented by NIM in May 1971[11] and in June 1972[12].

The development of fluidized-bed ion exchange with reverse-flow transport of resin has been pursued by the U.S. Bureau of Mines since the late 1960s[13–16], but their work has not yet progressed beyond the pilot-plant stage.

Today there is world-wide interest in the application of fluidized-bed ion-exchange technology to the recovery of uranium. Ritcey, Slater, and Lucas[17] and Streat and Quassim[18] published the results of laboratory studies, and, more recently, workers from Davy Powergas described their development programme[19, 20]. Pechiney Ugine Kuhlman have also been involved in a development programme, and are understood to have a small commercial plant in France that is handling slimes with a solids content of 6 per cent by mass. Alternative fluidized-bed approaches are the Porter system[21], which is being commercially operated by Rössing Uranium Ltd, the horizontal tank system suggested by Lloyd[22], and the Himsley column[23]. Although the Himsley system is rather ingenious, its operation is complicated.

South African Programme

As shown in Table I, the overall South African programme for the development of continuous ion exchange and its application to the recovery of uranium is, and has been, a collaborative effort between NIM, the Extraction Metallurgy Division of the Atomic Energy Board (AEB), the uranium industry, and the chemical industry.

This paper discusses the parts of the programme concerned with the recovery of uranium under the main headings Engineering, Process, and Plant Design.

Engineering

The plant that has evolved from the programme of research is now well known and has been described in a number of publications[24–27]. It is essentially a cylindrical tower divided into a number of contacting stages that are separated by trays for distributing the liquid. Each stage contains resin, the volume of which is determined by the requirements of the process.

The feed solution is pumped into the bottom of the tower and flows upwards, fluidizing the resin in each stage and leaving the tower by a simple overflow launder. During the period of solution flow, the resin beds expand to the height of each stage, the tower is fully flooded with resin, and there is no wastage of volume.

The resin flows countercurrent to the solution. It is fed to the column and moves through it intermittently, control being achieved by the use of synchronous timers. Slugs of resin leaving the bottom stage are collected in a closed bin, known as the transfer bin, where they are isolated in readiness for transfer to the second column. The transfer of resin from bin to column is done under hydraulic pressure.

At the beginning of the engineering programme, it was decided that all the development should be done on a relatively large scale. Up to that time, only small laboratory-scale models had been built, and it was quite clear that large-scale equipment would be required if the engineering aspects of the system were to inspire confidence. Thus, a hydraulic mock-up with a diameter of 1,8 m was built in 1969.

The objects of the engineering development programme were as follows.

(a) To develop the hydraulic characteristics of the

TABLE I

THE DEVELOPMENT OF CONTINUOUS ION EXCHANGE IN SOUTH AFRICA AND ITS APPLICATION TO THE RECOVERY OF URANIUM

Main topic		Detailed projects	Work completed or stopped	Work in progress or planned	Responsibility for investigation			
					NIM	AEB	Gold–uranium industry	Chemical engng industry
Engineering development of the CIX contactor		Hydraulic tests in 1800 mm CIX rig to establish parameters for mechanical design	×		×			
		Further simplification of tray design and ancillary circuits (valves, pumps, resin-transfer vessels, etc.)		×	×			
		Instrumentation and control circuits for resin movement and process operation		×	×			
Application of CIX to gold-recovery flowsheets		Details not shown		×	×		×	
Application of CIX to the recovery of zinc		Details not shown	×		×			×
Application of CIX to uranium-recovery flowsheets	Unclarified solutions	Tests in 600 mm CIX pilot plant on strong-base resins with nitrate elution	×			×	×	
		Tests in 250 mm pilot plant with strong-base resin circuit and H_2SO_4 elution	×			×	×	
		Proving of CIX and strong-base resin circuit in 2500 mm-diameter demonstration plant	×			×	×	
		Commissioning of full-scale CIX plant in CCD-CIX-SX circuit*	×			×	×	
	Slimes	Tests by the Chamber of Mines on counter-current cyclone washing followed by direct treatment of cyclone overflow by CIX	×				×	
		Tests on the Relix process, involving uranium recovery by ion-exchange resins directly in the leaching vessels	×			×	×	
		Trials with slime feed to 600 mm CIX pilot plant	×			×	×	
		Development work on cyclones and other sand–slime and solid–liquid separation techniques		×		×	×	
		Development work on slime feeds to CIX rigs		×		×		
		Proving of integrated circuits for slime feeds to 2500 mm CIX demonstration plant with heavy resin		×		×	×	×
	General	Development of analysers for uranium in resins and solutions for CIX control circuits		×		×		
		Laboratory and pilot-plant investigation of weak-base resin circuit using chloride solution		×		×		
Development and evaluation of new and improved ion-exchange resins for recovery of uranium		Laboratory and on-plant testing of resins from manufacturers of commercial resins		×		×		
		Laboratory testing of a high-density ion-exchange resin for uranium applications		×		×		×
		Testing of a high-density resin in the 250 mm CIX pilot plant with unclarified solution as feed		×		×		×
		Testing of a high-density resin in CIX rigs fed with slimes to evaluate hydraulic parameters, etc.		×		×		×
		Proving of a high-density resin in the 2500 mm CIX demonstration plant with a slime feed		×		×	×	×
		Studies on the effects of Si, Cl, SO_4, pH, etc. on the loading and elution of resins		×		×	×	×

*Circuit incorporating countercurrent decantation, continuous ion exchange, and solvent extraction.

Continued on next page

TABLE I— (Continued)

Main topic	Detailed projects	Work completed or stopped	Work in progress or planned	Responsibility for investigation			
				NIM	AEB	Gold-uranium industry	Chemical engng industry
Development of methods for design and costing of CIX plants (including scale-up)	Development of new and improved mathematical models for process design		×	×	×	×	
	Development of techniques for process design, costing, and flowsheet optimization		×	×	×		
	Compilation of a general engineering design manual for CIX		×	×			
	Evaluation of scale-up parameters		×	×	×		
	Radio-active tracer tests in CIX columns		×		×		
Design and costing of CIX plants for specific gold applications	Details not shown		×	×		×	
Design and costing of CIX plants for specific uranium applications	Laboratory and pilot-plant tests to obtain process design parameters		×		×	×	
	Process design and costing studies for individual mining groups and companies in South Africa		×		×	×	
	Compilation of a process design manual and data source book for uranium applications		×		×		
	Economic comparison of CIX circuits with conventional resins and those with high-density resins		×		×		×
	Design and costing studies for CIX applications in other countries		×		×		
Development of new and improved ion-exchange resins	Fundamental work on development of new and improved resins (metal-specific resins, high-density resins, etc.)		×	×		×	×
	Fundamental investigation of kinetics, mechanisms, and poisoning of resins		×	×		×	
	Review of existing bench-scale procedures and equipment for testing of resins and development of improved techniques		×	×	×		
Evaluation of new and improved ion-exchange resins for platinum, gold, and copper	Details not shown		×	×			

distribution trays in each stage so that the fluidization of the resin beds would be stable and that there would be no bypassing of the resin beds.

(b) To develop a simple control technique for resin transport and so ensure that the stages would remain full of resin under all conditions and would never become depleted. Depletion of the stages had been observed in earlier designs and constituted a major criticism of the column system.

(c) To develop the cycle of resin flow so that movement of the resin in and out of the column would be stable under all conditions.

(d) To develop control systems that would ensure balanced conditions when two or more columns were linked to form a recovery module.

(e) To develop the general dimensions of the system and so achieve a plant that could readily be adapted in size to suit any required throughput.

Although it was known at the time that continuous ion exchange was workable as a process, it was clear that these five points were vitally important if what was essentially a laboratory concept was to form the basis of a stable operating plant.

Design of the Distribution Tray

It is generally recognized that fluidized-bed systems, because the particles are in constant motion, can be scaled to much larger diameters than packed-bed systems without the danger of maldistribution of the fluid. This, of course, assumes that the bed is evenly fluidized, which is largely dependent on the pressure drop across the flow-distribution system, whether it is a system employing a perforated plate or a pipe manifold. An important aspect of the column design of fluidized-bed ion-exchange plant is that the fluid is redistributed at each stage so that the flow at the top or barren end of the column (the most critical) is almost perfectly uniform. Mass transfer is therefore good, and

TABLE II

EFFECT OF CYCLING ON RESIN INVENTORY – WITH CAPS

Flow-rate of solution 1,9 l/min
Flow-rate of resin 0,98 l/min
Fractional volume of resin transferred 0,9

Cycle	Resin inventory in each stage at end of cycle (% of volume at start of run) Stages				
	1	2	4	5	6
1	95,0	97,5	100,0	100,0	101,0
2	95,0	99,5	100,0	100,0	101,0
3	93,5	99,5	100,0	100,0	100,0
4	97,5	99,5	100,0	100,0	100,0
5	101,0	101,0	100,0	99,5	99,0
6	97,5	99,5	99,0	99,0	99,0
7	93,5	99,5	99,5	99,0	99,0
8	97,5	97,5	96,5	99,0	99,0
9	99,5	99,5	99,5	100,0	99,0
10	103,0	99,0	99,0	100,0	94,5
11	103,0	99,0	98,5	100,0	94,5
12	93,0	99,0	94,5	100,0	94,3
13	97,0	103,0	99,5	100,0	93,7
14	98,5	100,0	99,5	100,0	95,0
15	98,5	100,0	96,5	100,0	97,0
16	98,5	100,0	97,5	97,5	98,0
17	93,5	99,0	99,5	96,5	99,0
18	94,5	98,0	99,5	97,5	99,0
19	95,5	98,5	97,5	97,5	97,0
20	97,5	99,0	96,5	96,5	98,0
21	99,5	100,0	97,5	96,5	97,0
22	97,5	100,0	99,5	94,5	99,0
23	93,5	99,5	100,0	99,5	99,0
24	93,5	103,5	100,0	99,5	99,0
25	93,0	99,5	100,0	99,5	99,0

TABLE III

EFFECT OF CYCLING ON RESIN INVENTORY – WITHOUT CAPS

Flow-rate of solution 1,9 l/min
Flow-rate of resin 0,9 l/min
Fractional volume of resin transferred 0,9

Cycle	Resin inventory in each stage at end of cycle (% of volume at start of run) Stages				
	1	2	4	5	6
1	100,0	100,0	100,0	100,0	100,0
2	89,2	90,1	90,1	90,0	78,4
3	88,2	94,0	87,1	80,0	83,3
4	78,4	97,0	81,2	84,0	88,2
5	78,4	91,1	87,1	88,0	87,3
6	70,6	89,1	84,2	85,0	86,3
7	70,6	87,1	88,1	85,0	83,3
8					
9	65,7	84,2	80,2	88,0	78,4
10	58,8	85,1	75,2	85,0	80,4
11	66,7	82,3	76,2	80,0	84,3
12	67,4	88,1	69,3	86,0	86,3
13	53,9	65,3	71,3	80,0	70,6
14	51,0	71,3	69,3	72,0	78,4
15	57,8	79,2	73,3	77,1	84,3
16					
17					
18	60,8	68,2	69,3	70,0	93,1
19	60,8	82,2	67,3	69,0	88,2
20					
21	68,6	64,4	67,3	70,0	88,2
22	68,6	64,4	67,3	70,0	88,2
22					
23					
24					
25	63,7	89,1	63,4	70,0	88,2

The resin inventory for runs 8, 16, 17, 20, 22, 23, and 24 was not taken.

resin losses due to surges are minimized. In addition to considerations of pressure drop, the size of the hole, and its pitch and fabrication must be taken into account. A workable design has been developed, as is demonstrated by the successful operation of a column 4,25 m in diameter. Indeed, the commercial plants of this design appear to be more stable than the various pilot plants that have been operated.

Control of Resin Hold-up in the Stages

Depletion of resin in the stages has been eliminated by the development of a simple cap that is placed over each perforation of the bottom tray and is arranged to give a pressure drop similar to that across the rest of the stages (Fig. 1).

The cap works on the principle that, during a reversal of flow, the resin immediately leaves all the stages that are separated by perforated plates and enters the stage below. However, the caps force the resin from the bottom stage to move by a longer path, delaying it before it drops into the conical bottom. Thus, at the end of the reverse-flow period, less resin has been transferred from the stage above the bottom tray than from the other stages, and the resin in that stage is above the equilibrium volume established during the previous solution-flow period. However, this accumulated resin is redistributed over the column once the flow of solution recommences, and thus the hold-up in each stage is maintained.

Tables II and III compare two runs on a laboratory column (100 mm in diameter) containing seven stages. One run was done with caps on the bottom stage, and the other with a simple perforated plate, all the other stages being separated by perforated plates. The effect of the caps is clearly shown. The concept of the cap has been patented[11] and has proved very successful in commercial operation.

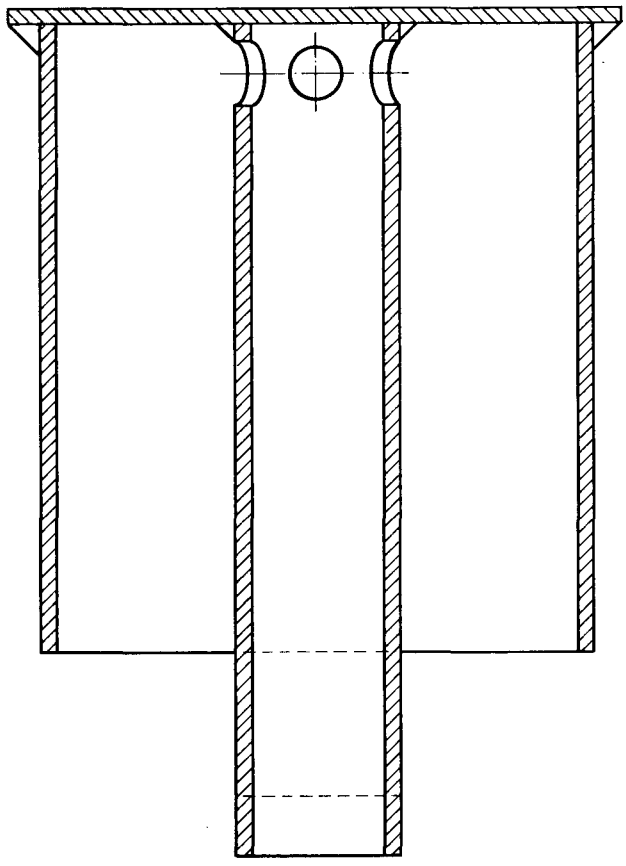

Fig. 1—A typical cap used in the bottom stage

Resin-transport Cycle

The concept of a reversal of flow to achieve interstage transport of the resin is now generally well known. In the early stages of development, it emerged that the transport of resin through the trays is predictable and consistent. These two points are particularly important and have been put to use in the establishment of the overall cycle of the column. This cycle comprises five steps and can be summarized as follows.

(i) *Forward-flow period.* Solution flows up through the column, thereby fluidizing the beds of resin contained in each stage.

(ii) *Settling period.* The flow of solution is shut-off, and the resin is allowed to settle to the bottom of each stage so that the transfer of resin in a dense state is ensured during the following period, and the back-flow of solution between stages is minimized.

(iii) *Reverse-flow period.* A known volume of solution is allowed to drain from the column by way of the transfer bin. This drainage causes a known volume of resin to transfer between the stages, resin from the bottom stage moving into the transfer bin.

(iv) *Delay period.* Solution continues to circulate through the bottom of the column and the transfer bin. This circulation ensures that all the resin remaining in the bottom of the tower after the reverse-flow period is moved through to the transfer bin.

(v) *Resin-transfer period.* The transfer bin is isolated from the column, and the slug of resin transferred into it is lifted to the top of the second column under hydraulic pressure. This transfer takes place during the forward-flow period.

In addition to ensuring stable movement of resin, this sequence ensures that no valves close on the resin, and that the movement of resin is gentle, thus keeping attrition losses to a minimum.

General Plant Dimensions

The general dimensions of ion-exchange plants need to be considered separately for each particular case, and little can be discussed here. The most important aspect in establishing the general shape and dimensions of the column is the flared top. This flaring reduces surging during the introduction of the resin slugs, and so prevents entrainment of resin in the overflow.

Process

It is clear that the introduction of continuous ion exchange to uranium extraction has made no difference at this stage to the chemistry of the ion-exchange process. The object of the process-development work that was conducted together with the engineering programme was to establish the feasibility of continuous ion exchange on a scale larger than that of the laboratory, and to evaluate its long-term operating performance with respect to various points such as plant reliability,

process efficiency, treatment of unclarified feeds, resin attrition, resin poisoning, and reagent usage.

As mentioned earlier, the main object in the development of continuous ion exchange was to relax the constraints placed on the solid–liquid separation plant. The only significant work has been carried out on so-called unclarified solutions, which contain about 300 to 500 p.p.m. of suspended solids. Only preliminary work has been conducted on slimes, and investigations are still proceeding. Flowsheets for slimes are therefore not discussed in this paper.

Three basic flowsheets have been investigated at various scales of operation:

(1) a strong-base resin circuit with nitrate elution,
(2) a weak-base circuit with nitrate elution, and
(3) the Bufflex or Eluex circuit, which is a combination of ion exchange and solvent extraction.

A fourth flowsheet — a weak-base resin circuit with chloride elution — is being studied in the laboratory.

Strong-base Resin with Nitrate Elution

This is the flowsheet that was used in South Africa before the advent of solvent-extraction technology. Its adaptation to continuous ion exchange is depicted in Fig. 2. The ion-exchange section of this flowsheet was tested during the campaign at Hartebeestfontein on a pilot plant of 600 mm diameter. The results have been published elsewhere[26], but it is worth recording the main conclusions here. The object of the test run was to compare the capacity of the continuous plant with that of the main plant operating under similar conditions. The conditions set were from 0,002 to 0,003 g of U_3O_8 per litre of barren solution, and from 8 to 10 g of U_3O_8 per litre of concentrated eluate. These conditions were achieved with a flow-rate of pregnant solution of 5,9 m^3/h per cubic metre of wet-settled resin. The comparative figure for the main plant was 2,6 m^3/h per cubic metre of wet-settled resin, indicating that the continuous plant has more than twice the capacity of an equivalent fixed-bed plant.

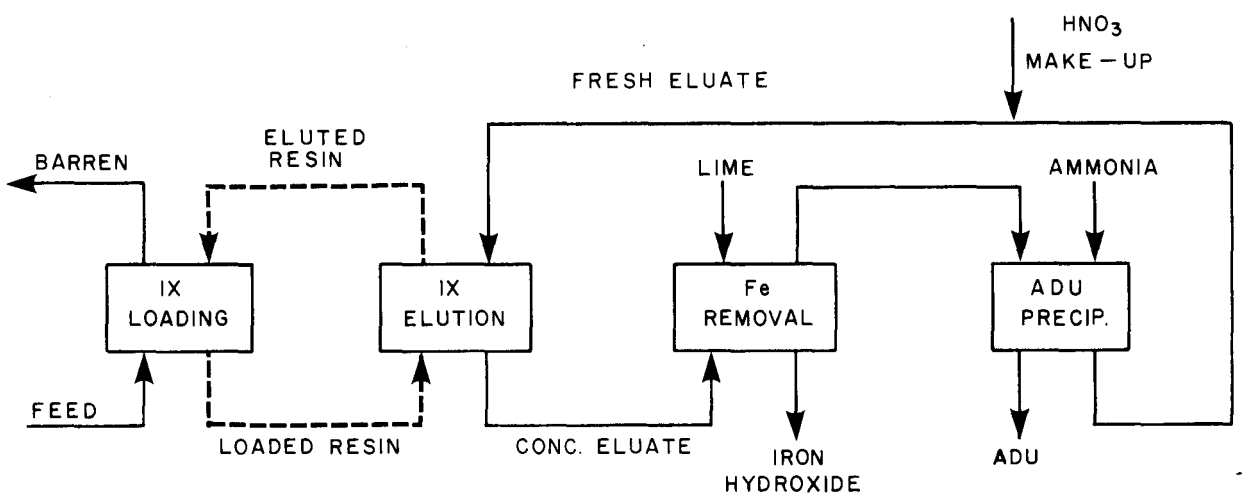

Fig. 2—Flowsheet using a strong-base resin and nitrate elution

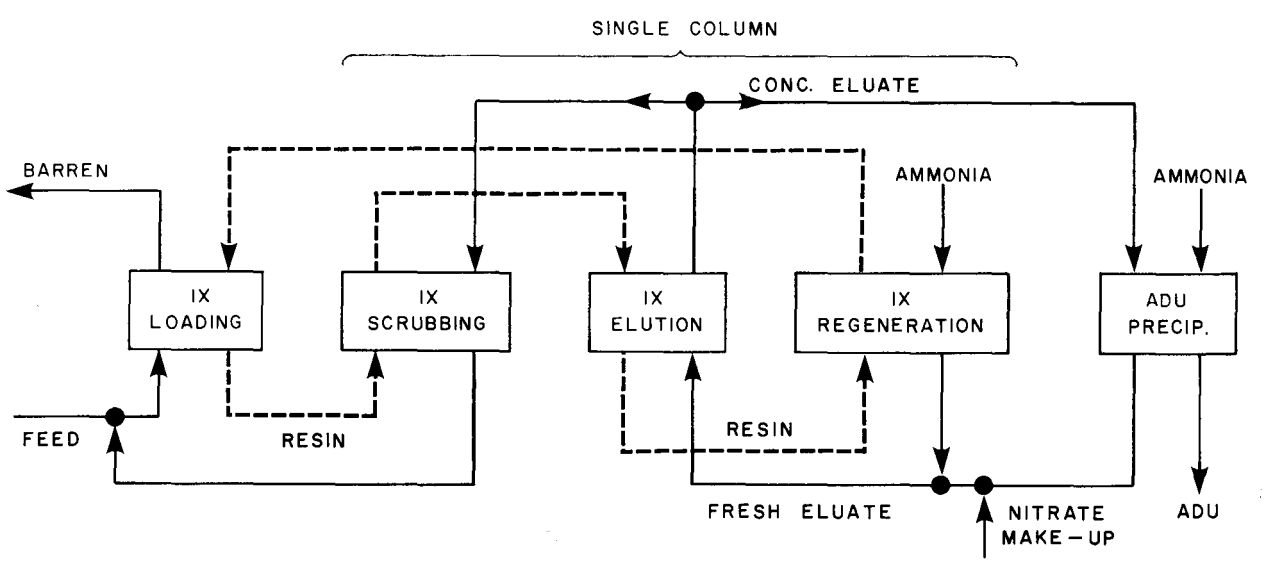

Fig. 3—Flowsheet using a weak-base resin and nitrate elution

TABLE IV

ADU ANALYSIS — WITHOUT NITRATE RECOVERY

Constituent	Main plant using IRA-400	Pilot plant using XE-299	Solvent extraction
U_3O_8, %	92,42	94,6	96,03
SO_4, %	3,20		3,40
SiO_2, %	1,52	0,06	0,03
Al, p.p.m.	1,000	< 3	20
As, p.p.m.	90	< 3	< 10
B, p.p.m.	13,9	6	0,7
Ca, p.p.m.	3,600	—	150
Cd, p.p.m.	< 1	< 0,3	< 1
Co, p.p.m.	< 3	4	< 10
Cr, p.p.m.	20	< 10	3
Cu, p.p.m.	30	12	0,3
Fe, p.p.m.	2,000	300	140
Mg, p.p.m.	50	60	10
Mn, p.p.m.	200	30	5
Mo, p.p.m.	16	50	4
Ni, p.p.m.	< 3	5	< 1
Pb, p.p.m.	< 3	6	< 3
Sn, p.p.m.	2	< 3	2
Ti, p.p.m.	< 3	< 3	< 3
V, p.p.m.	< 1	< 1	1
Zn, p.p.m.	< 10	< 30	< 10

Weak-base Resin with Nitrate Elution

The development of this flowsheet formed the major part of the campaign in the 600 mm-diameter pilot plant[26]. The campaign had as its object the establishment of a flowsheet that would give an ammonium diuranate (ADU) product of equivalent purity to that produced by the solvent-extraction process. The basic flowsheet is given in Fig. 3.

The object was almost achieved, as can be observed from Table IV, but only with the introduction of a displacement scrubbing system[26]. The use of this technique, however, led to an unacceptably high consumption of nitrate. Furthermore, when the nitrate was recovered by the use of ammonia, the product was found to contain unacceptably high levels of silica, which was due to the partial removal of silica from the resin by the ammonia. In view of these problems, the use of weak-base resins is not recommended at this stage.

In other respects, the weak-base resin is most acceptable. Good loading and elution efficiencies were achieved, although at a reduced flow-rate as a result of the slower

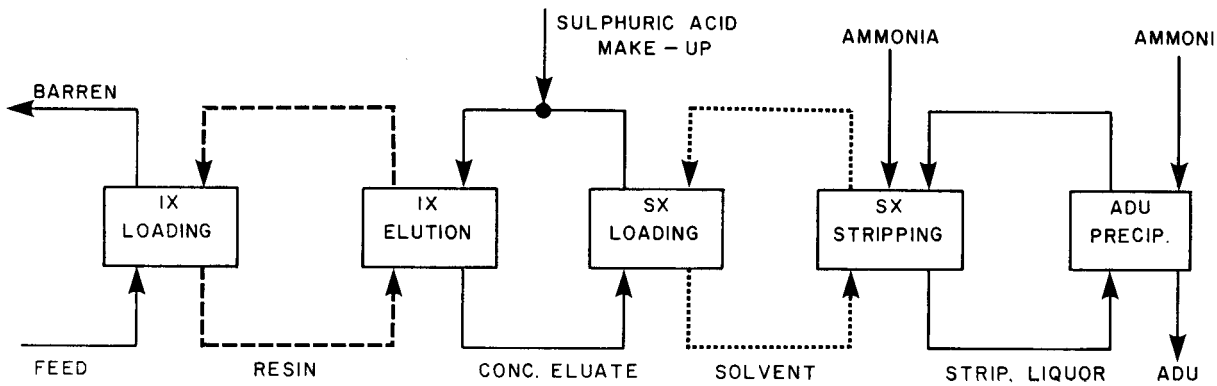

Fig. 4—Flowsheet for the Bufflex process

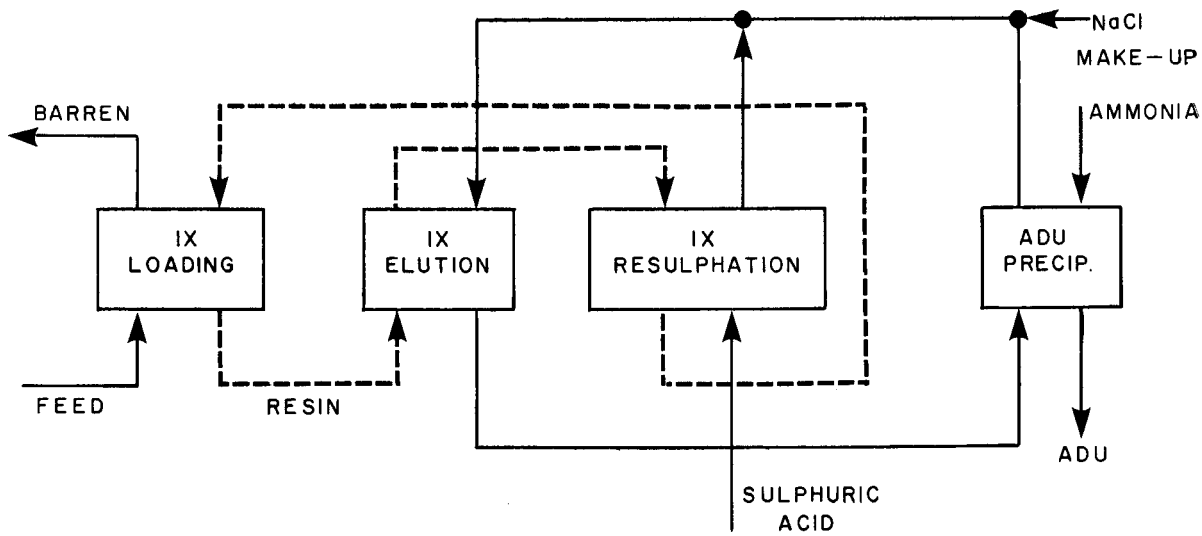

Fig. 5—Flowsheet using a weak-base resin and chloride elution

loading kinetics of the macroporous resins that were used.

A factor observed during this campaign, and one that had a significant effect on the testwork, was the unusually high rate of fouling of the macroporous weak-base resins by silica. There is still some controversy as to whether the high rate of fouling is due to the functionality of the resin or due to its structure. Recent testwork seems to indicate that the more important parameter in the rate of silica fouling in pregnant solutions of uranium is structure.

The Bufflex Flowsheet

Owing to the difficulties in the adaptation of weak-base resins to the extraction of uranium (mainly economic), the development programme reverted to the use of strong-base resin but modified to the Bufflex system[1], in which the ion-exchange plant upgrades the pregnant solution, making it more acceptable economically for solvent-extraction processing. The basic flowsheet is given in Fig. 4. Most of the development of this circuit, which combines two processes, was done on a demonstration plant of 2500 mm diameter. This work forms the subject of another paper[28] and will therefore not be discussed here.

Weak-base Resin with Chloride Elution

This flowsheet (Fig. 5), which is used at two U.S. uranium plants[29, 30], is being evaluated on a laboratory scale. This flowsheet has possibilities, but there are a number of considerations to be taken into account particularly with respect to the consumption and cost of reagents, the quality of the ADU product, losses of chloride to the main circuit, and materials of construction. It does, however, offer the potential of a pure product in a single step.

Plant Design

Once a basic flowsheet has been chosen, the next step is the establishment of the design and size of plant that will give the desired recovery and eluate concentration. The basic mechanical components have already been discussed, and this section is confined to a discussion of the current approach to the establishment of basic process conditions in relation to the loading column. The elution column can be designed similarly, but procedures have not reached as advanced a stage as for the loading section.

In the process design the variables that need to be fixed are

(a) the diameter of the column,
(b) the height of each stage,
(c) the resin inventory in each stage,
(d) the number of stages, and
(e) the flow-rate of the resin.

Diameter of the Column

The determination of the diameter is based on hydraulic considerations, and involves a determination of the expansion characteristics of the resin under consideration.

Experience has shown that the upper limit for bed expansion should not be greater than 3 for resins of standard column grade. If the bed expansion is greater than this, losses of fines become excessive. With resins of the grade used in resin-in-pulp processes, higher expansion is possible. Because the expansion of a bed resin depends on the loading of uranium, the expansion will be greatest in the top stage, and, for this reason, tests on expansion should be done with eluted resin in barren solution. The diameter of the column is estimated from the superficial velocity, which gives the desired bed expansion for the top stage. A velocity of 18 m/h was used in the design of the demonstration plant[28].

Height of Stage

Although the height of the stage is considered to be an independent variable in the design calculations and is fixed at some practical value, it is possible to optimize its value. For large columns, in which access to the stages could be necessary, a minimum stage height of 1 m is recommended.

Number of Stages

The number of stages required for any recovery is determined by the following method.

(1) The inventory of resin in each stage is estimated from the height of the stage, the diameter of the column, and the bed expansion of the eluted resin,
(2) The concentration profiles are calculated for solution and resin.
(3) The inventory of resin in each stage is adjusted to account for the dependence of bed expansion on resin loading.
(4) The profile is recalculated until convergence is reached.

The calculation procedure is numerical, and is based on a knowledge of the kinetics of mass transfer, the equilibrium between solution and resin, and the periodic operation of the column. Models are used to describe the equilibrium and the kinetics, and all that are required for a design are laboratory-determined data on the equilibrium and kinetics.

It is not the intention to discuss here the modelling of the column because the models are still under development and details will be published at a later date. However, a comparison between the results of design simulations and the operating data is worth while.

Fig. 6 compares measured and predicted concentration profiles for the demonstration plant (diameter 2500 mm) and the pilot plant (diameter 250 mm). These two plants were operated in parallel at the same time and under the operating conditions shown in Table V. The conditions were exactly the same for both plants, except that the volume of resin transferred out of the pilot column per cycle was inadvertently set at 18 litres instead of the scaled-down value of 16,5 litres. This naturally led to the pilot unit having a more favourable profile and a lower resin loading than the demonstration plant, and it thus gave a better extraction. The important point, however, is that the model used was capable of predicting both profiles from the same laboratory data and that the predictions in both cases compared favourably with the measured profiles.

Flow-rate of Resin

The flow-rate of resin is determined by material balance once the required recovery and the maximum

loading for the resin in equilibrium with the pregnant solution are known. Two methods for the control of resin flow are possible:

(a) variation of the volume transferred per cycle for a fixed cycle time, and
(b) variation of the cycle time for a fixed volume transferred per cycle.

In general, it is preferable to transfer a volume as close to the stage hold-up as possible. The maximum possible mass transfer performance is achieved when the ratio of resin transferred to stage hold-up is 1. In practice, the resin loading is set at about 75 per cent of the equilibrium value.

The Elution Column

The detailed modelling of the elution column has not yet been completed, and the present approach to its design is therefore based on simple residence time derived from practical experience. The time required for complete elution is determined in the laboratory by the use of a single fluidized-bed stage similar to that used in the determination of the adsorption kinetics.

In the determination of the size of the elution column, the following factors are taken into account:

(1) if possible, the elution column is made the same height as the adsorption column so that construction and operation are simplified,
(2) a minimum of five stages is recommended to reduce by passing, and
(3) an expansion of the resin bed of not less than 1,2 is used for stability.

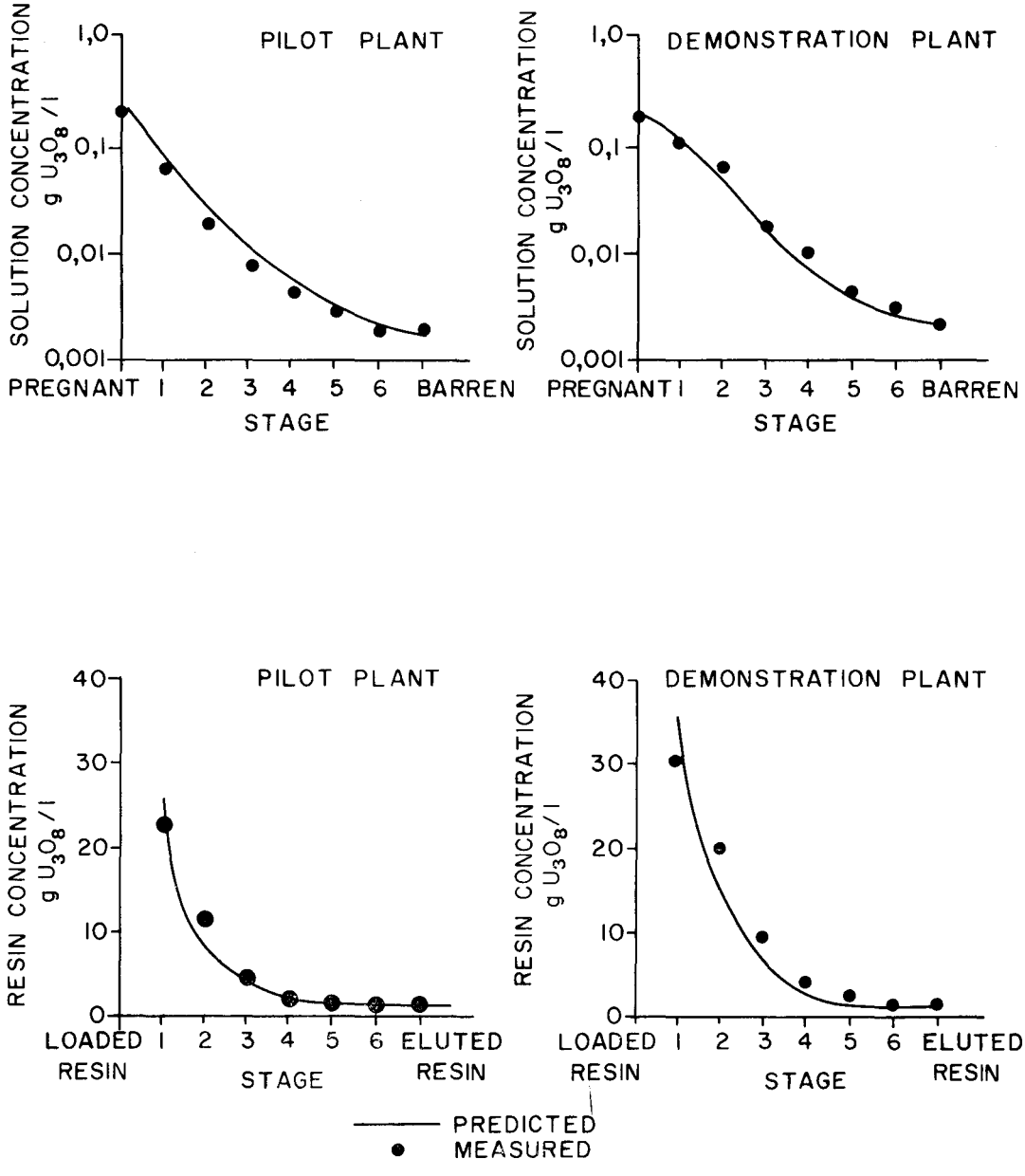

Fig. 6—Comparison of measured and predicted concentration profiles

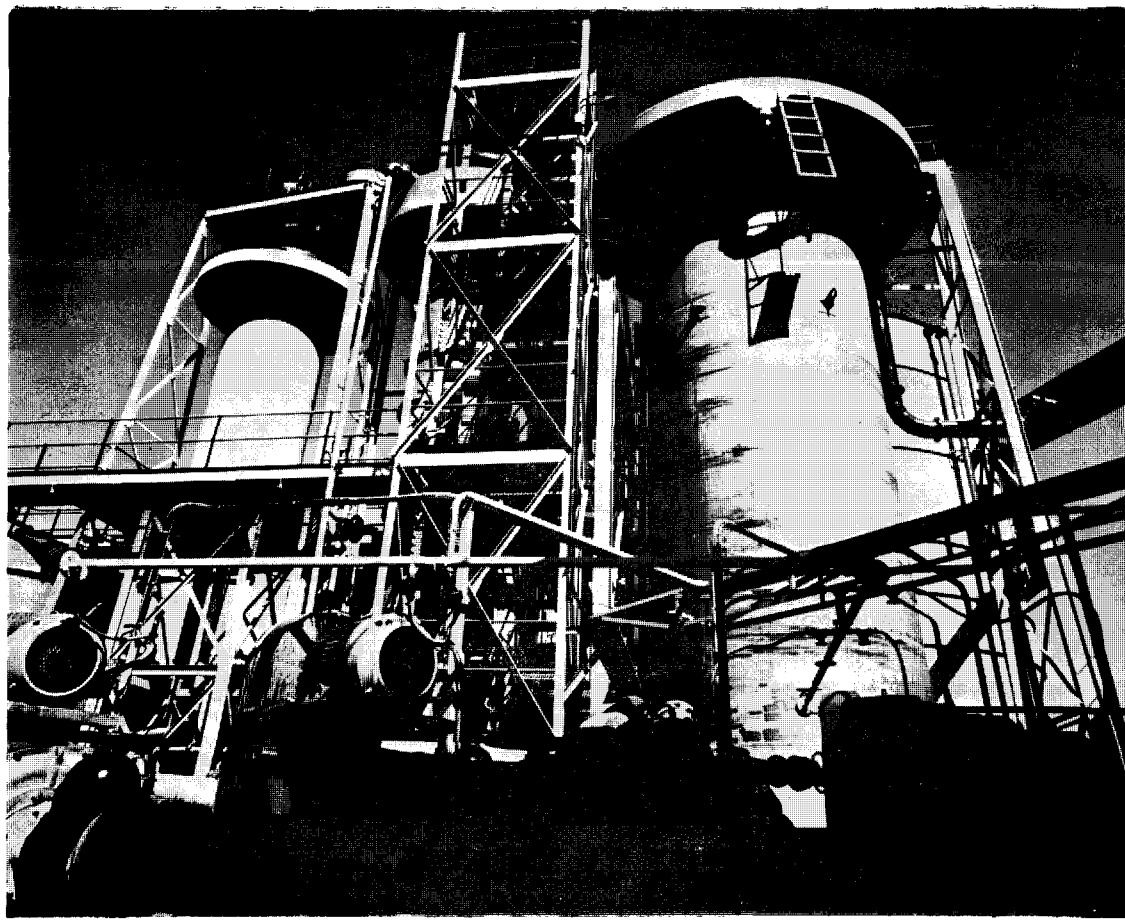

Fig. 7—General view of the first full-scale commercial continuous-ion-exchange plant in South Africa

TABLE V

OPERATING DATA FOR TEST CAMPAIGN ON THE DETERMINATION OF SCALE-UP PARAMETERS

Column	Pilot plant	Demonstration plant
Diameter, m	0,25	2,5
Stage height, m	0,93	1,0
Forward-flow period, min	180	180
Settling period, min	1	1
Reverse-flow period, min	4	4
Delay period, min	5	5
Transfer period, min	20	20
Flow-rate of solution, l/min	14	1424
Vol. of resin transfer, litre	18	1650
Resin	Duolite A101 DU	Duolite A101 DU

The design models used in the evaluation of the number of contacting stages are based on certain assumptions pertaining to the mixing patterns of both the resin and the solution phases. It is policy to continually update and improve these models, and the measurement of the mixing patterns by means of radioactive tracers has been undertaken. These tests have yielded interesting results and will be published at a later stage. In general, however, they indicate that the assumptions used in the models are conservative and that segregation of the resin is insignificant, which is of considerable importance in the scale-up of a continuous ion-exchange system.

Conclusion

The initial aim of the programme — the development of a commercially acceptable plant that would relax the constraints placed on the solid–liquid separation process — has been achieved. This is demonstrated by the recent successful operation of a full-scale commercial continuous ion-exchange plant (Fig. 7). In this application, the ion-exchange system has been successfully incorporated in a Bufflex process flowsheet, which is now regarded, technically and economically, as the most advanced process for the recovery of uranium in South Africa.

The Future

Although the initial object has been achieved, the research programme has gone only part of the way. Up to the present, relatively clear solutions (about 300 p.p.m. of suspended solids) have been handled, and it is obvious that still greater benefits could be obtained if the system could be adapted to feed solutions containing much higher levels of solids.

Some preliminary work was carried out in 1974 in the 600-mm-diameter pilot plant in which slimes with a solids content of up to 10 per cent were treated successfully. This limit was determined by the denisty of the commercially available resins. Attempts have been made to produce heavy ion-exchange materials[10, 31], but the

heterogeneous materials that were synthesized have not achieved commercial success owing to problems of chemical and physical instability. An entirely new concept is under development, which involves a homogeneous organic ion-exchange resin that has been produced with sufficient density to allow for the treatment of feeds with a solids content of 20 per cent and that has kinetic and equilibrium properties similar to the resins commercially available. This resin should open up a whole new generation of process flowsheets.

In addition to the development of flowsheets for heavy resins and slimes, work is being undertaken on the engineering of the system and the design procedures.

Materials of construction have not been discussed because the optimum choice of materials has not formed part of the development programme. With the present flowsheet, the two sections of the plant can be separated with respect to materials of construction: the loading section, which has to be designed to treat large volumes of very dilute solutions of sulphuric acid (pH 1,5 to 2) at ambient temperature and, in certain instances (e.g., in applications in the Orange Free State), solutions containing significant quantities of chloride; and the elution section, which has to handle, at temperatures of up to 50 °C, 10 to 15 per cent solutions of sulphuric acid that contain traces of solvent.

The materials of construction recommended at present are 316L stainless steel for the loading section and fibreglass-reinforced plastic (GRP) for the elution section. Although successful in operation, these materials have a number of disadvantages including the following.

(a) Both are expensive.
(b) Stainless steel cannot be used in the presence of high levels of chloride.
(c) There is a lack of expertise and experience in the fabrication of very large GRP vessels in South Africa.

It is therefore essential that experience in GRP fabrication should be built up rapidly in South Africa. Alternatively, modifications should be made to the design of the distribution trays to allow for the use of rubber-lined mild steel, including solvent-resistant types. This is probably still the cheapest material of construction for vessels that need to be resistant to sulphuric acid.

The following are further points worthy of consideration:

(1) simplification of the valving and pumping systems,
(2) development of washing techniques for the resin, and
(3) development of an improved design of transfer bin.

Acknowledgements

The contribution of all those involved in the development programme is gratefully acknowledged. The programme has been in progress for over eight years, and many members of staff of NIM, AEB, and industry have contributed to the work. To single out any names would therefore be very difficult. However, particular acknowledgement is made of the unfailing assistance and cooperation of the managements and staffs of the mines on which the pilot-plant testwork was carried out.

The permission granted by NIM, AEB, and the uranium industry (Nuclear Fuels Corporation of S.A. Ltd) to publish this paper is also gratefully acknowledged.

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